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Project Title: Research into Protective Coating Systems for Outdoor Bronze Sculpture and Ornamentation, Phase III.

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Executive Summary

The ultimate goal of this three-phase research project was to develop new coating strategies through an increase in understanding of how coatings for outdoor bronze sculpture and ornamentation work and fail. The immediate objective of Phases II and III of the project was to determine the weathering performance of five medium to high performance coating systems, previously tested in Phase I, on four typical bronze or copper-alloy substrates. The evaluation of these metal/coating systems, spread over the second two phases of the project, included chemical, physical, and electrochemical impedance methods after both accelerated and natural weathering. Overall failure ratings were compiled through visual evaluation of various properties according to appropriate ASTM standards, combined with digital analysis of corrosion after weathering. In this report, recommendations concerning protective coating options and practices as they relate to outdoor bronze sculpture and ornamentation are based on overall performance ratings and analytical results of Phase II samples.

Introduction

Every outdoor bronze work of art is a unique case scenario, that is, has its own history in terms of materials, manufacture and outdoor exposure. Thus, it is unrealistic to expect that one solution may exist to universally satisfy the aesthetic requirements and protective function of coatings for outdoor bronzes. Yet, these expectations are often encountered in the fields of art and conservation. Furthermore, the conservation approach to metal objects in outdoor exposures must be based on a different set of criteria than that relied upon for indoor museum objects. This is because exposure to aggressive, polluted outdoor urban environments in which bronzes are often found may subject these materials to chemical/electrochemical instability, often resulting in disfiguring changes in appearance. In many cases, visual changes are unforeseen by the artist. Thus, conservative notions of non-aggressive intervention in the fate and appearance of an object must often be abandoned if an object is to be protected and preserved.

In the final analysis, surface preparation, coating choice, and maintenance planning remain the subjective property of conservators, who, with curatorial and scientific input, must find a difficult middle ground of an aesthetically acceptable option that does not compromise the object in terms of stability in the harsh setting of outdoor

urban environments. The coupling of corrosion science, polymer science, and interfacial chemistry, along with aesthetics, render the subject of coatings for outdoor bronze sculpture and ornamentation complex and difficult to approach for conservators and scientists alike. At best, one may hope to identify and reach a better understanding of the relative roles of different factors in coating appearance and durability in the outdoor environment. For this reason, the present study has paid particular attention to the interplay of adhesion, thickness, coating quality, and pretreatment with the corrosion inhibitor BTA in overall performance. Other factors, such as coating permeability and bulk coating composition, have also been considered. The picture painted by this research serves in one sense to underline the complexity of this network of factors. It is hoped that the research will serve as an aid to finding the “weak link” in systems comprised of bronze, an organic coating, and outdoor exposure conditions, and thus to aid in informed decisions about appropriate coating strategies.

This research project has been comprised of three phases. In Phase I, 29 different coatings systems were weathered on two types of substrates: polished, cast monument bronze and 50-year-old copper roof. The latter substrate was chosen as an excellent example of a natural, brochantite patina. These patinas cannot be reproduced exactly in a laboratory and are essentially the same as those formed on bronzes. Weathering of the Phase I samples was both natural, on the roof of the National Gallery of Art, and accelerated in the laboratory using UV exposure and an acid rain-type solution, coupled with cyclic, broad range exposures of temperature and humidity.¹ This type of accelerated weathering was modeled on methods used in the automotive industry.

In Phases II and III of the project, five of the coatings deemed most viable were chosen for further study in a new round of natural and accelerated weathering on an expanded range of substrates. The substrates are: a) polished, cast bronze; b) artificially patinated, polished, cast bronze; c) 50-year-old copper roof, and d) the same copper roof material after walnut shell-blasting. The five coatings systems are: 1) two coats of Incralac with a wax topcoat, 2) benzotriazole (BTA) pretreatment plus wax, 3) an acrylic, acrylic urethane, and wax layered system (G.J. Nikolas & Co. coatings), 4) BTA pretreatment with BASF acrylic urethane and wax topcoat, and 5) a two-coat Nikolas waterborne acrylic urethane plus wax. By choosing a small number of representative substrates and coatings for study, Phase III of the research focused on the importance of substrate preparation and substrate composition in the choice of a protective coating. Results in Phases II and III also seek to repeat and clarify results of Phase I. The present report should be considered as an extension of Phase II results and conclusions, contained in the “Final Report to the National Center for Preservation Technology and Training 1997 Grant Program.”²

Experimental Methods

Sample Preparation and Testing

The complete description of all Phase II sample materials, their manufacture, analysis, and preparation, as used in Phase III of this study, is contained in the 1997 Final Report. All coatings were applied according to normal conservation practices. The following is a summary of pertinent information about composition and manufacture of

the coatings. Incralac, manufactured by StanChem, Inc., is an unpatented formulation made from Acryloid B-44, a thermoplastic methyl methacrylate copolymer; the corrosion inhibitor benzotriazole (BTA); and a silicone oil. The wax used in this study is formulated by Nicolas Veloz, an outdoor sculpture conservator. It is a blend of about 75% Bareco Victory Wax (microcrystalline, synthetic, low melting point wax), plus Bareco Polywax 2000 and 500 (polyethylene microcrystalline waxes), and Petronauba C, an oxidized polyethylene wax. This coating has no BTA. All waxing consisted of two brush coats followed by light buffing. The Nikolas 11565 Outdoor Lacquer is a “modified acrylic” lacquer designed for exterior brass and bronze, and is supplied ready for use. The manufacturer reports that this coating contains BTA as well as UV absorbers. Nikolas 9778 Exterior Uralac is a room temperature cure, two-component acrylic urethane developed for exterior lighting, exterior hardware, automotive trim, exterior signage, and sporting goods, including gold-plated, brass, and silver-plated metals. The manufacturer confirmed that this coating contains BTA and other UV absorbers. BASF Glassodur-MS Top Clear 923-85 is a two-component, high solid acrylic urethane formulated from a proprietary acrylic copolymer crosslinked with a trimer of hexamethylenediisocyanate (HDI). The manufacturer reports that this coating contains BTA. Nikolas 11560 Eco-borne Brass Lacquer is a one-component, waterborne acrylic urethane. The manufacturer confirmed that the coating contains BTA, but no additional UV absorbers.³

The description of the accelerated weathering protocol for sample set B can also be found in the 1997 NCPTT report. Phase II, sample set C was naturally weathered on the roof on the National Gallery for just over one year. The samples were placed facing due south at a 45° angle according to ASTM G7. Adhesion testing and dry film thickness determination were done in accordance with ASTM standards D3359 and D1400, respectively. This testing protocol is also described in the 1997 NCPTT report.

Overall Performance Ratings

Coating performance was first assessed on the weathered samples through visual evaluation. The visual ratings were broken down into the following categories: a) texture change (including surface spotting/ etching), b) flaking/peeling, c) hazing or whitening, d) blistering/ cracking/ checking (ASTM D714, D660), e) color change. Each of these categories were ranked on a scale of 0-5, where: 0=not present; 1=barely noticeable; 3=noticeable; 4=very noticeable; 5=dramatic. Color changes on weathered and unweathered samples was measured by a HunterLab Ultra Scan XE spectrophotometer. The color change was identified using the delta E cmc system, which calculates changes in terms of perceptible color. Because color change during weathering of a clear coating over metal involves change in the coating as well as the metal surface, and is therefore highly complex, visual analysis was found to be the superior method of evaluation. The color data measured with the spectrophotometer, as well as the digital image analysis results, were used as aids in the visual evaluation of color ratings.

Digital imaging and analysis were performed to assess overall corrosion and to measure corrosion at the scribe mark on all of the weathered samples. Photographs of the bronze and copper plates were captured and then scanned as 32-bit images. All of the images were taken with a color strip and ruler within the frame of the photograph. The Scanalytics, Inc. software program IPLab for Macintosh, version 3.2, was used to

quantify the percent corrosion on each plate, as well as at the scribe marks. For corrosion analysis, the software defines a selected area of the image on the weathered plates according to the color parameters red, green, blue, yellow, magenta, cyan, hue, intensity, saturation, or value. Up to three of these parameters can be combined to define a specific color. However, this is also a limitation of the program, since the range of colors found on the different samples is quite varied, and the corrosion is not uniform, thus defying general definition by only three parameters. In addition, the metal plates themselves may contain mottled surface coloring and colors similar to those in the corrosion. It was therefore necessary to individually tailor the color parameters on each coating and substrate for corrosion identification. However, even with these modifications, it was found that significant error remained in the quantification of overall corrosion by digital analysis, except in the case of polished bronze. Therefore the scale defined in ASTM D6 10 was used to determine the percent corrosion over the entire surface in place of digital analysis results. However, the digital images were found to be very good aids in judging percent corrosion in this manner. Percent overall corrosion, which did not exceed 33% on our coated samples, was added straight into the rating as a numeric percent value (allowing that 50 was a maximum value).

Mean linear corrosion at the scribe marks was measured by digital image analysis, and reached a maximum mean of 3.76 mm for these samples, although some maximum values ranged close to 16 mm. For the digital analysis of scribe corrosion, a one-pixel line was drawn down the center of each incision of the “X” scribe. A “measure length” function was used to draw a perpendicular line from the inscribed line to the edge of the scribe corrosion. This was done on either side of the inscribed line at eleven evenly spaced positions, totaling 88 readings per plate. The mean length of the lines was calculated by the software and converted into millimeters. In order to normalize values to a 1-25 scale for the overall failure rating, measured values were multiplied by a scalar of 6.25. This method was found to greatly increase the accuracy of scribe corrosion measurement.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is ongoing at North Dakota State University on a set of coated, polished bronze samples which had already undergone accelerated weathering at the National Gallery of Art (Phase II set B), as well as a set of unweathered, coated polished bronze plates (Phase II, set A). For the latter samples, the most evenly coated areas were chosen for measurement; after an initial set of readings, measurements have been subsequently taken on the same spot between cycles of accelerated weathering. The coupling of an accelerated test method with EIS provides analysis of the coating breakdown during weathering. The weathering pattern consists of a two-week cycle, fashioned according to ASTM D 5 894-96 *Standard Practice for Cyclic Salt Fog/UV Exposure of Painted Metal (Alternating Exposures in a Fog/Dry Cabinet and a U V/Condensation Cabinet)*. In the first week, the samples are placed in a QUV® cabinet where they are exposed to four hours of exposure to 340 nm UV-A at 60 °C, alternated with 4 hours of condensation at 50 °C. In the second week, the samples are placed into a Prohesion® Chamber that cycles between one hour of salt fog at 25 °C and one hour of no fog at 35 °C. The salt fog used for weathering is dilute Harrison’s solution (0.35 wt. % $(\text{NH}_4)_2\text{SO}_4$ and 0.05wt. % NaCl in H_2O). EIS measurements are

taken twice a week using a Gamry Instruments PC-3 Potentiostat. The EIS measurements are taken using a removable 1.5 inch (outer diameter) glass tube with an o-ring clamped to the bronze plate. The glass tube is filled with the dilute Harrison's solution, and a saturated calomel reference electrode and a platinum counter electrode are immersed into the solution. The amplitude applied to the system is 5 mV, and the frequency range is from 0.1 Hz to 10,000 Hz.

Removability

Removability tests were conducted on Inralac on the various substrates with and without weathering according to established protocol, as follows. Mixtures of cyclohexane and toluene were applied to the film surface with cotton swabs. Approximate solubility of the Inralac film was determined by using a mixture consisting of 1 ml of the less polar solvent and a quantity of the more polar solvent added in 0.1 ml increments from 0 to 1 ml. Subsequently, a more accurate test involved using 4 ml of the less polar solvent with the incremental addition of the more polar solvent once again in 0.1 ml amounts. This process was continued until reaching a point at which the Inralac adhered to the cotton fibers. Rather than touching the entire swab to the paint surface, three to five fibers were teased from the cotton wool and left trailing from the swab tip. Only the trailing cotton fibers were allowed to rest on the film surface, thus minimizing mechanical removal of the material. A topcoat of wax, whenever present, was removed by gently wicking it away from the spot to be tested using a cotton swab wetted with cyclohexane. The mixture at which dissolution of the coating first occurred was reported in terms of the solvent strength. Solvent strength, in the absence of a third solvent such as acetone, is simply the percent toluene in the cyclohexane/toluene mixture.⁴

Infrared Spectroscopy and Ellipsometry

Reflection-absorption infrared spectroscopy (RAIR) was performed on thin films of Cu(I)BTA formed on rolled bronze by immersion in solutions of either a) 1.5 wt.% BTAH/ethanol, b) 3.0 wt.% BTAH/ethanol, or c) 1.5 wt.% BTAH/water. For this purpose, a Bio-Rad Digilab FTS-60A Fourier transform infrared spectrometer fitted with a Harrick versatile reflection attachment for center-focused beam and a retro-mirror accessory, plus a wire-grid polarizer set for parallel beam polarization, were used. The angle of incidence of the parallel-polarized beam was in all cases 78 degrees. Samples were purged with dry air for 10-20 minutes in order to minimize the absorption of atmospheric moisture. The spectra were obtained from an average of 1024 scans at a resolution of 4 cm⁻¹ and recorded in absorbance. The final surface reflection spectrum for each sample was obtained by digitally subtracting a spectrum of the cleaned bronze sample taken before immersion in the BTAH solution and placed with the same geometry in the accessory before and after treatment. In cases of very long immersion in BTAH solutions, sample spectra were also produced by subtracting that of a new, freshly scanned, untreated rolled bronze coupon. In some cases, the latter results were superior and were utilized in the reported data. Absorbance at 745 cm⁻¹ was calculated by the WIN-IR software from the maximum height of this peak to a baseline drawn between 835 to 729 cm⁻¹.

Solutions of BTAH (Aldrich, 99%) were made with HPLC-grade ethanol or millipore, distilled and deionized water. The pH of aqueous BTAH solutions was 5.30.

Solutions were made at least 12 hours prior to use. The rolled bronze was manufactured by Lubaloy Co.; it is spring-tempered, 425 bronze, 0.016 gauge. The alloy composition is: 88.5% Cu, 9.5% Zn, 2% Tin. Rolled bronze samples were prepared by polishing with a series of Micro-mesh cloths (6000, 8000, and 12000 mesh). A small group of samples were polished starting with 2400 mesh for improved results. The polished samples were wipe-cleaned first with “Acryli-clean” (PPG Industries, Inc.), then wiped and rinsed with HPLC ethanol several times until substrates passed the water-break test. Small pieces were cut from the polished, cleaned metal, immersed into the appropriate BTAH solution for the prescribed length of time, and then immediately rinsed in an ethanol bath for 5 minutes, followed by rinsing with a stream of ethanol and air drying.

Ellipsometry was performed on the experimental Cu-BTA films at the University of Cincinnati using a Rudolph Research Inc. Thin Film Ellipsometer, type 43603-200E. Film thickness was calculated from measurements of the delta and psi parameters using a film refractive index of 1.6. In this method, an uncoated bronze coupon served as the background, so that the thickness of the natural cuprous oxide layer was subtracted from Cu-BTA thickness measurements.

Attenuated total reflection (ATR) spectroscopy is ongoing and has been used to further investigate the polymer/metal interface of selected coatings. For this purpose, the coating was delaminated from the metal substrate by immersion in liquid nitrogen, or simply peeled off when possible after accelerated weathering. ATR was performed with a Harrick 4x beam condenser fitted with a delrin holder for SPP crystals with faces measuring 10 x 5 x 1 mm. The IRE crystals used in this study were KRS-5 45°, KRS-5 60°, and Ge 45°. Calculated depths of penetration for these crystals were, respectively, 2.92, 1.56, and 1.53 micrometers.⁵ For samples that were smaller than the crystals, multiple samples were placed together on the holder and exposed areas were masked with aluminum foil. ATR spectra were corrected for wavelength dependency using the “atrcorr.ab” function in the Grams 32/Win-IR software.

Gas Chromatography

Gas chromatography analysis was performed on extract from size AD 3B English walnut shells, the copper patina, and the walnut shell-blasted copper patina. Each of the samples was immersed in methylene chloride to extract the fatty acids and left overnight. The solvent was pulled off, filtered through a 0.45 μ m filter and dried with a nitrogen stream. According the methods of White and Pilc, 25 μ l of TMTFTH (m-trifluoromethyl) phenyltrimethylammonium hydroxide, 5% in methanol) was added to the remaining solute in order to derivatize the sample for GC analysis.⁶ This reagent converts fatty acids, in free acid and glyceride ester forms, to their methyl esters. One μ l injections were made into a Perkin Elmer Autosystem GC, in splitless mode, with a Restek Rtx-1 column and flame ionization detector. The temperature was programmed at 50 °C for 0.5 minutes, then increased at 25 °C/min. to 100 °C, and then at 6°/min to 280°C, held for 5 minutes. The injector temperature was 300°, and the detector temperature was 325 °C. Data was processed using Turbochrome software.

Results and Discussion

Overall Failure Ratings

Subsequent to accelerated weathering, preliminary overall failure ratings of Phase II, set B samples were compiled for the 1997 NCPTT Final Report.⁷ This report also includes failure ratings for Phase I, set C samples, i.e., after 1.5 years natural outdoor weathering. These ratings were determined by combining individual corrosion and coating ratings according to set criteria from appropriate ASTM standards. The component ratings were weighted to best correspond to empirical rankings. Adhesion ratings before and after accelerated weathering, and dry film thickness, were also reported in the 1997 report. In this report we present revised failure ratings for all Phase II samples. These failure ratings are similar, but now based on the results of digital image analysis combined with visual evaluation. The revised ratings are also compared to electrochemical impedance tests for the samples on polished bronze. Revised overall failure ratings for Phase II samples after 120 days accelerated weathering (set B) are shown in Figure 1, and after about one year natural, outdoor weathering (set C) in Figure 2. Note that three samples placed on the roof from the polished bronze series disappeared during the course of the experiment and are therefore not represented. Since natural weathering was not much progressed after one year in most cases, description of these samples is included in Table I. Photographs of the naturally weathered samples are also attached.

The failure ratings for sample sets B and C are a product of three main components: a) coating condition, b) overall percent pitting corrosion, and c) mean linear creepage corrosion at the scribemark. All visual evaluation was rated in terms of change after weathering, as described in Experimental Methods. In this formulation, the maximum possible coating failure comprises 25% of the total failure rating, overall pitting corrosion comprises 50%, and scribe corrosion comprises the remaining 25%, for a total possible score of 100%. This weighting arose empirically and matches that used in the preliminary failure ratings. Overall corrosion was weighted more heavily since this type of failure ultimately represents inability of the coating to protect the substrate. It is felt, however, that overall corrosion more directly relates to permeability properties of the coating, although it does not represent the whole picture. The scribe corrosion appears to more directly correspond to adhesive properties of the coatings by exposing the interface between the coating and the substrate. The coating condition represents aesthetic problems that may arise upon weathering, such as color change or whitening, as well as evidence of more fundamental property changes, such as blistering or cracking. The latter may be preludes to corrosion and peeling.

Digital images and analysis of Phase II control samples (unweathered), plus the Phase II samples after weathering, are described in Experimental Methods. It was necessary to write individual algorithms for each of the four types of bronze and copper roof substrates in order to analyze the samples. Due to difficulty in defining overall pitting corrosion on the various substrates with the software, the digital images were used mainly as an aid to obtain the ASTM D6 10 standard value for percent overall pitting corrosion. This combined method resulted in considerably improved ratings over the ASTM method, using the eye with or without magnification. On the other hand, the digital image analysis produced precise measurement of mean linear creepage corrosion

at a scribemark; these results were normalized to an appropriate scale, then used directly in the overall failure ratings.

General Observations

This rating process led to relatively low overall percent failure ratings, since none of the coatings failed across the board in all categories. The ratings should thus be viewed as sensitive to conservation standards in that any perceptible visual change is noteworthy. In this respect, a failure rating of 10-20 indicates perceptible failure in at least one category, while a failure rating of 40-50 (or more) clearly represents an unacceptable degree of failure.

As seen in both Figures 1 and 2 where results are grouped by substrate, coating performance was highly dependent on the type of substrate. This is particularly true of two substrates: the patinated bronze and the walnut shell-blasted copper roof. In these cases, especially the artificially patinated bronze, coatings generally performed worse in both accelerated and natural weathering tests. On patinated bronze, the three worst performers in accelerated weathering, i.e., the BTA/wax, acrylic/acrylic urethane/wax, and BTA/acrylic urethane/wax, show above normal change in the coating layer itself, particularly in terms of blistering, as well as a large amount of peeling and scribe corrosion. This may be due to a possible degradative influence of the patina's iron and nitrate salts on the coatings, as well as to corrosion-induced de-adhesion. The BTA pretreatment, when present, has no apparent effect on inhibiting oxidation of the surface. The untreated, uncoated patinated bronze surface was even observed to oxidize to blackish colored products in room conditions. In addition, scanning electron microscopy of the artificial patina on bronze samples⁸ previously revealed a patchy, finely cracked mineral layer, which undoubtedly contributed to poor adhesion in the system. The patina in fact appeared to be loosely adhered to the bronze, since the top surface was rubbed off a small bit when cleaning with a paper towel. The substrate itself may thus be said to be unstable for coating.

On the walnut shell-blasted copper roof, other than the wax the poor performance of coatings rose in part from scribe corrosion. The scribes mostly appeared to have dark green haloes, suggesting reprecipitation of the brochantite here from moisture/electrolyte ingress.⁹ Adhesion of the coatings, as measured at room conditions, did not appear to be much impaired, however (see Figure 5). The implication is that adhesion under wet conditions was poor in these systems. As reported previously,¹⁰ scanning electron microscopy /energy dispersive spectroscopy (SEM/EDS) of the walnut shell-blasted surface showed an aggravated porosity and non-homogeneity in the patina layer, as well as the new presence of carbonaceous material. Evidence in the analysis of this substrate was conflicting in terms of the presence of residual oil from blasting, however. The presumed residue of walnut oil from the blasting could not be confirmed either by FTIR of the patina nor by gas chromatography (GC) of patina extracts. While GC positively identified walnut oil from extractions of the shells used for blasting, results from patina extractions both before after blasting contained many acids, so that positive identification of walnut oil was not possible by this method. In either case, the above evidence indicates that the substrate was significantly destabilized in terms of corrosion potential.

Apart from differences in the substrates, one may generalize that both the BTA/wax coating and the waterborne acrylic urethane performed poorly or in a mediocre

fashion on all substrates after accelerated testing. It was noted that the wax coating performed relatively better on the unblasted, 50-year-old copper roof substrate in both accelerated and natural tests. This may be ascribed to the ability of the wax to penetrate into and mechanically adhere to the natural mineral patina, making a more effective matrix (see Final Report, 1997). In this way the wax may actually fortify the existing protection of the natural patina, making it more resistant to acid rain. The drawbacks of waxing an existing patina are, however, not to be discounted. These may include significant color change of the object, difficulty of future removal, and significant accretion of dirt and soot in the outdoors. Although not evidenced on these samples, wax coatings are also infamous for developing whitened areas that may flake off. This behavior was noted on thicker wax coatings of the same material used in Phase I (see Final Report, 1997).

On the remaining substrates, BTA/wax coatings had the above drawbacks plus allowed severe overall pitting corrosion in the form of light green, powdery spots to develop. This result was especially remarkable on the walnut shell-blasted copper roof substrate, where removal of a significant portion of the natural patina apparently resulted in a vulnerable surface on which the wax coating provided entirely insufficient protection.” Furthermore, results after slightly more than one year of outdoor weathering show that the waxed samples (excluding the absent polished bronze) are beginning to pick up in signs of deterioration. Upon examination under magnification, the waxed, polished bronzes in Phase I showed etching beneath the wax after relatively short exposures in the outdoors. The Phase I samples, despite a much thicker wax coating of the same material, also performed poorly in accelerated and natural weathering.¹²

Overall failure ratings also show that the solvent-borne acrylic urethane coatings generally performed well across the board, except on the patinated bronze substrates. The good performance may be attributed to low moisture and ion permeability, as well as excellent overall durability of the crosslinked coatings. Incralac with a wax topcoat also performed fairly well on two of four substrates: the polished bronze and the 50-year-old copper roof. This was despite mediocre adhesion and fairly thin coating application. Thus it can be said that all of the lacquer-type coatings in this study performed reasonably well on these substrates under the accelerated and natural weathering conditions used here.

The waterborne acrylic urethane coating, although boosted in thickness in this study, did not perform well in general and failed dramatically on the 50-year-old brochantite patina after one year of natural weathering, i.e., at an even faster rate than predicted by accelerated tests. The latter case appears largely attributable to the extremely poor adhesion measured on this substrate vs. the others. However, this coating was a mediocre performer in all cases, regardless of substrate. This points to an inherent weakness in the coating itself, such as too great an affinity for moisture/electrolytes arising from residual water in the coating, as well as generally poor coating quality, which could not be avoided despite following manufacturer’s recommendations during application.¹³ ATR spectra of this coating on polished bronze before and after weathering (not shown) show small relative increase in the free —OH stretch region, near 3535 wavenumbers, apparently confirming the uptake of moisture in the coating near the metal surface.

Comparison of Failure Ratings to Dry Film Thickness and Adhesion

Comparison of the overall failure ratings and results of film thickness measurements (Figure 3-4),¹⁴ shows a correlation to poor performance of the BTA/wax coating, which is a much thinner coating than the others: 0.2 mils or less. This thickness is typical of normal wax application in conservation practice, and may be said handicap its performance potential. Although the Nikolas acrylic/acrylic urethane/wax coating was applied somewhat more thickly than the others, and thus could have received a slight boost, this effect is not readily apparent. The remaining three coatings were in a similar thickness range, from 0.6 to 1.0 mil, which represents a typical sprayed coating thickness in conservation practice. Coating thickness was therefore determined to not be a major factor in the performance of our samples outside of the BTA/wax coating. As previously mentioned, however, application of thicker wax coatings such as studied in Phase I did not improve performance markedly.

Comparison of the overall failure ratings to adhesion tests of coatings before and after weathering (Figures 5-6) shows that the excellent measured adhesion of the BTA/wax coating had relatively little effect on its performance. The adhesion test results for wax appear to be an artifact, however, because the wax has very poor cohesive strength, but is so thin that any de-adhesion within the wax layer itself is difficult to observe by this method. Thus, measurements are artificially inflated. While the wax is excellent at forming mechanical adhesion on rough surfaces, this type of adhesion is not sufficient to offset the porosity of the wax coating, which allows access of an electrolyte such as acid rain or Harrison's solution to the metal surface.

The adhesion bar graphs also show that significant losses in adhesion occurred on patinated bronze during weathering of the acrylic and solvent-borne acrylic urethane coatings. This clearly accounts for a good deal of failure not seen on the other substrates, although it is unclear whether this dynamic loss of adhesion contributed to poor coating performance as a cause or effect. As previously mentioned, the artificial patina was only loosely adhered to the bronze, also contributing to the generally poor adhesion of the coatings before and/or after weathering and causing cohesive failure within the patina layer. This was apparent in areas that delaminated from the bronze and were seen to have the patina stuck to the delaminated side of the coating.

The almost non-existent adhesion of the waterborne coating on the copper roof samples may be due to poorer wetting of the coating on this substrate, which would result in little or no penetration into the patina.¹⁵ The poor adhesion in large part predicts the dramatic failure observed on the copper roof sample during natural weathering. On the other hand, it is quite interesting that the waterborne acrylic urethane on both the bronze substrates and the blasted copper roof actually gained some adhesion during weathering. This appears to explain the somewhat better performance of the waterborne acrylic urethane relative to the others at least on the patinated bronze. An explanation for the increased adhesion in these cases could be an interaction between the coating and metallic ions, causing increased curing or other strengthening properties. This should be investigated in future work.

Incralac and the Nikolas acrylic/acrylic urethane showed loss of adhesion on polished bronze with accelerated weathering, but this did not appear to affect their performance significantly, at least not at this point in the weathering. In the case of Incralac, ATR spectra of the polymer/bronze interface before and after weathering

confirm that chemical changes may occur at the metal/coating interface during weathering. As shown in Figure 7, a broad shoulder centered near 1690 wavenumbers is developing during weathering. This indicates the formation of carboxylic acids and carboxylate salts near the metal surface, which most likely account for corrosion-induced de-adhesion and forecast future problems.

Removability

Removability tests were performed for Incralac on the various substrates. In particular, information regarding any change in removability with weathering was sought. Results indicated that 11-13% toluene (in a toluene/cyclohexane mixture) was necessary to dissolve the Incralac on all of the bronze or copper samples, both with and without accelerated weathering. In other words, no significant increase in the polarity of the solvent was necessary to remove the coating after weathering on any substrate examined. Contrary to expectations from some reports in the literature,¹⁶ this suggests that no significant amount of crosslinking has taken place in the Incralac coating in any of these samples. The only difference noted in the tests was a slightly lower solvent strength (9% toluene) for dissolution of Incralac on a glass slide vs. on a copper alloy substrate. This result suggests that the copper substrate itself has some effect on the formation of an Incralac film, causing slightly greater end solids, greater entanglement, and/or greater order. The only difference noted in the tests was a slightly lower solvent strength (9% toluene) for dissolution of Incralac on a glass slide vs. on a copper alloy substrate. This result may be related to evidence of trapped toluene molecules still present in a one-year-old Incralac film on glass.¹⁷ This suggests that the copper substrate itself has some effect on the formation of an Incralac film.

EIS of Phase II Samples

Electrochemical test methods, primarily EIS, have recently moved center stage as important tools for the quantitative characterization of coatings on metal substrates.⁷ EIS is particularly valuable for the rapid ranking of coatings and prediction of future performance. In EIS, a given range of frequencies of alternating voltages is applied to an electrode, which in this case is the coated metal plate. The system may be defined by an equivalent circuit, in which the particular metal and coating represent various circuit elements, such as capacitors, resistors, and inductors. The measured time lag between the excitation ($V(t)$) and response signal ($I(t)$) is said to arise from characteristic types of frequency absorption or response to the applied voltage and the electrolyte. The impedance of the angular frequency is equal to the ratio $V(t)/I(t)$, and the impedance modulus is a sum of the real and imaginary impedance. The Bode plots in Figures 8 and 9 (discussed below) show the impedance modulus $|Z|$ (ohms) vs. frequency (Hz). EIS is being used in this study as a parallel method of coating evaluation.

Interpretation of Bode plots presents a valuable picture of dynamic changes taking place in the coating/metal system during progressive weathering and reveals a wealth of information about the coating itself. Low frequency impedance is thought to arise mainly from resistance to wetting at the metal surface beneath the coating pores; loss of impedance at the low frequency end is then interpreted as loss of wet adhesion, i.e., replacement of adhesive bonds with moisture.¹⁹ According to Funke and others,²⁰ wet adhesion should be considered distinct from dry adhesion, which is known to be a

relatively poor predictor of coating performance in the presence of water. Thus, at low frequency, the impedance can be considered a measure of the coating's resistance to the electrolyte, so that higher impedance values indicate a more protective ability of the coating in general.

Other interesting features of the Bode plots are the high frequency response and the shape of the impedance curve. Decreases or flattening in the slope of impedance vs. frequency may be interpreted as increasing non-homogeneity in the coating, such as the formation of microcracking, while decreases in the impedance modulus at the high frequency end are thought to indicate increasing porosity in the coating.²¹ In addition, increases in impedance modulus with weathering are commonly interpreted as the formation of new corrosion or other passivating layer.

Preliminary EIS work was previously conducted on five polished, cast bronze samples from Phase I. The five coatings tested were: a waterborne acrylic urethane (StanChem, Inc.), Incralac, Incralac + wax, BTA pretreatment + Incralac, and BTA pretreatment + wax. Visual changes to the samples during testing were noted but not taken into account in the rankings. These results, reported in the 1997 Final Report, indicated a benefit in performance from BTA pretreatment for a limited period of time, after which performance fell markedly. The ranking order from EIS preliminary results also showed that a wax topcoat boosted performance, although much less so than BTA pretreatment.

Further EIS, coupled with a more realistic accelerated weathering protocol than simple immersion in dilute Harrison's electrolyte, has been performed on Phase II coated, polished bronze samples (set A, controls) for 98 days and is ongoing. Periodic measurements have been taken on samples between cycles of salt fog in a Prohesion® chamber and QUV® exposure, i.e., during progressive, artificial weathering, as described in the Experimental section. For the purpose of comparison, a single set of EIS measurements were also made on coated, polished bronze samples that had already undergone accelerated weathering at the National Gallery of Art.

The impedance modulus $|Z|$ at 0.1 Hz is plotted against time/cycle of weathering for sample set A in Figure 10. The uncoated sample has $|Z|_{0.1 \text{ Hz}}$ between 10^2 and 10^3 ohms. This marks the effective point of failure, when the coating no longer exceeds the impedance of the uncoated metal. Coatings that have impedance $|Z|_{0.1 \text{ Hz}}$ above 10^7 ohms are considered to be performing well under this weathering protocol. As seen in Figure 10, after 91 days of weathering only the Nikolas acrylic/acrylic urethane/wax and the BTAIBASF acrylic urethane/wax coatings remain in this category.

Figure 10 also illustrates that the impedance of the coatings does not fall sequentially with time, but rather oscillates up and down. This phenomenon arises from moisture cycling in the weathering regime. After one week in the Prohesion® chamber, if the coating has imbibed quite a lot of moisture, the metal at the bottom of the pores is wetted and conductivity increases. This causes the impedance to drop. When the sample is again exposed to QUV®, the moisture evaporates and the impedance rises. Two of the coatings exhibit large oscillations in impedance with weathering cycles: Incralac and the waterborne acrylic urethane. This indicates that these coatings, especially the latter, are vulnerable to moisture/electrolyte ingress. Although not readily shown on this graph, this was also true of the wax coating.

In one instance, impedance did not rise after QUV® exposure: the wax coating at 7 days. This suggests that moisture was actually trapped beneath the coating, in part explaining the rapid formation of corrosion that has been observed on the wax-coated samples. In fact, EIS readings for the BTA + wax-coated sample were discontinued after only 26 days because of its rapid failure. It should be noted that the initial impedance reading of the wax coating was less than 10^4 ohms, which is already very poor. Thus the wax coating does little to effectively block moisture/electrolyte ingress. Another noteworthy feature of the graph in Figure 10 is the temporary increase in impedance that is observed for the wax coating after 14 days. This may be interpreted as the formation of a new passivating layer at the metal/coating interface, most likely formed by the reaction of copper ions with chlorides and/or oxygen. When this layer subsequently breaks down after 26 days, impedance drops again. In addition, the Bode plot of the wax coating in Figure 8 shows a decrease not only in low frequency impedance with time of weathering, but a decrease also at high frequency. This indicates significant increase in porosity in the film. The Bode plot shows that after only eleven days of exposure to the weathering cycle, the BTA/wax coating failed. Results thus underscore the fact that this wax coating is in a different performance category altogether than the other coatings tested in this study. Thus, the BTA/wax coating cannot be considered to be truly protective.

Phase II, sample set A are presently in their fourteenth week of cycling between UV and salt fog exposure in the North Dakota laboratory, and will continue until they reach complete failure. The respective Bode plots (Figure 8) reveal the following ranking, in order of worst to best: BTA + wax (#2) < waterborne acrylic urethane + wax (#5) < Incralac + wax (#1) < BTA + BASF acrylic urethane + wax (#4) ≤ Nikolas acrylic/acrylic urethane/wax (#3). This ranking is identical to the overall failure rating ranking for the blasted copper roof substrates, but differs from the ratings on the other substrates, including that for polished bronze. However, it should be added that failure ratings of coatings #1, 3, 4, and 5 were tightly grouped on the polished bronze after 120 days accelerated weathering at the National Gallery of Art. It is possible not only that the weathering protocol caused a difference in ranking, but also that a spread in the performance grouping is better predicted by EIS. This is particularly true of the waterborne acrylic urethane, for which the $|Z|_{0.1 \text{ Hz}}$ value drops precipitously between 35 and 42 days. Thus the EIS results appear to predict the dramatic failure of the waterborne coating on the naturally weathered polished bronze and 50-year-old copper roof. Furthermore, the $|Z|_{0.1 \text{ Hz}}$ value for Incralac + wax begins to waver under 106 ohms after 42 days. Again, this may better predict eventual loss in adhesion and failure on polished bronze than seen in the accelerated weathering protocol at the National Gallery. Loss of adhesion in Incralac coating systems after weathering was also found on sample set B, as well as Phase I samples (see Figure 2 and 1996 and 1997 Final Reports to NCPTT).

EIS measurements additionally show that both the Nikolas acrylic/acrylic urethane system and the BTA+BASF acrylic urethane system are able to maintain a $|Z|_{0.1 \text{ Hz}}$ close to that of their initial readings during 98 days of accelerated weathering. These coatings clearly belong to a “high performance” category by EIS standards. In particular this is true of the Nikolas system, which exhibits almost no change in curve in the Bode plot (Figure 8). The BASF system Bode plot shows some leveling off of the

impedance modulus slope over time, suggesting the beginning of formation of microcracking in the coating. This behavior is borne out in the graph in Figure 10, where the Nikolas system $|Z|_{01 \text{ Hz}}$ remains fairly flat up to 77 days, and the BASF system starts some moisture cycling around 49 days.

The Bode plot for samples previously weathered at the National Gallery of Art is shown in Figure 9. EIS rankings to date are, from worst to best, as follows: BTA pretreatment + wax (#2) < uncoated bronze << Nikolas waterborne acrylic urethane + wax (#5) < BTA pretreatment + BASF acrylic urethane + wax (#4) \leq Nikolas acrylic + Nikolas acrylic urethane + wax (#3) \leq Incralac + wax (#1). These results correspond quite well with the overall failure ratings shown in Figure 1, especially with regard to the close ranking of the acrylics and acrylic urethane coatings. EIS also confirms that, except for wax, the other four coatings were performing marginally well after 120 days of accelerated weathering at the National Gallery of Art. A disturbing result shown here is that the waxed samples actually fell behind the uncoated sample, which is now covered by a coherent layer of corrosion.

The fair correspondence between EIS results of the two sets of samples indicates that the weathering protocols followed in the two laboratories are basically comparable, although weathering at the North Dakota laboratory appears to have been somewhat harsher and more accelerated. EIS may thus predict behavior further ahead than the accelerated weathering conducted at the National Gallery. It is interesting in this respect that the Nikolas acrylic/acrylic urethane system seems to best correspond in EIS ranking after both types of weathering. This supports the notion that the coating has the best stability of the five on polished bronze. Coatings that fail by EIS, however, such as the wax, waterborne acrylic urethane, and Incralac, appear to predict breakdown in protection that, in the case of Incralac, may not be yet evident in accelerated or natural weathering tests. The appearance of an increased acceleration factor in the EIS weathering protocol, as compared to accelerated methods used at the National Gallery of Art, may be ascribed in large part to a greatly increased “time of wetness” in the salt fog equipment. In the absence of automated fogging or spraying equipment at the National Gallery, approximately 5 minutes of hand spraying followed by 4 hours of 85% relative humidity did not equal the wetness achieved by 4 hours of direct fogging. Other differences in the accelerated weathering methods, such as the composition of the “acid rain” solution and duration of other cycles, are also important. On the other hand, the EIS experiments do not take into account any visual changes in the coatings, as was done in the overall failure ratings. It must be emphasized that no method of accelerated weathering or performance evaluation will ever produce outdoor exposure exactly, which in any case is site specific. This underscores the importance of comparing results of different methods of weathering as well as different methods of analysis in the general evaluation of coating performance.

Additional RAIR and Ellipsometry of CuBTA films

CuBTA films were investigated by reflection-absorption infrared spectroscopy (RAIR) and ellipsometry. Results have been written up and submitted for presentation/publication in the IIC 2000 Conference scheduled in Melbourne, Australia for October 2000 (Appendix A). Results suggest that CuBTA film thickness increases as a function both of immersion time and BTA solution concentration, and that ultrathin CuBTA films, as often produced in conservation treatments, provide extremely limited

and insufficient protection of the metal. Some evidence is provided that thicker CuBTA films formed during pretreatment may have a more positive effect on corrosion inhibition in outdoor exposure.

Conclusions and Recommendations

Understanding of coating performance must begin with an understanding of the substrate's nature and properties. A polished bronze substrate is a pristine, vulnerable surface with more potential for corrosion. A 50-year-old copper sulfate patina (brochantite), on the other hand, represents a partially passivated surface, whose subsequent corrosion will occur at a relatively slow rate but may also be subject to reprecipitation of the patina or new pitting corrosion. Perhaps more importantly, the mineralization creates a visually changed and physically rough, highly porous surface with a small amount of organic material incorporated.²² Two substrates studied in this project were found to be particularly unstable: the artificially patinated bronze, formed from ferric nitrate and most likely ammonium sulfate, and the walnut shell-blasted, natural brochantite patina on the copper roof. The artificially patinated surface was not only rough and uneven,²³ but also chemically unstable in terms of oxidation and, most likely, corrosive or degradative agents. In addition, the artificial patina appeared to be poorly adhered to the metal surface itself, most likely contributing to the generally poor adhesion of the coatings before and/or after weathering. The walnut shell-blasted substrate was found to be also rough and porous, but more uneven than the natural patina before blasting. There was also an organic material present on this substrate which could neither be removed by cleaning nor identified. These two substrates represent difficult situations for which to find satisfactory coating solutions and which should be avoided if possible.

As is well known, scrupulous surface cleaning of a metal surface leads to better coating adhesion and performance. Of utmost importance is also the skill and practice in coating application so that a coating of good quality and appropriate thickness is laid down with minimal defects such as seeds, solvent popping, pinholing, or orange peel. Results of this study reaffirm these commonplace rules as general aids in coating strategy. In addition, very thin layers CuBTA as often formed by minimal treatment with BTA appear to be severely limited or of little value in protection of the bronze. The use of a BTA pretreatment, where a relatively thick CuBTA underlayer is deposited, may help delay the onset of corrosion once moisture and salts permeate a coating. The use of wax topcoats generally appears to boost coating performance and has the added benefits of covering many coating defects and matting shiny surfaces. However, whitening of this wax layer was sometimes observed in accelerated weathering, so that maintenance of such a top layer may be required. Assuming good substrate preparation, the use of acrylic urethanes, which are truly high performance coatings, may be an option in some cases. Removal of these crosslinked coatings may present special problems, however, as discussed below.

The picture presented in these failure ratings is thus one of a complex interaction between the coatings, the substrate, their history and their environment. One way to view this tangle of factors is to look for weak links in the system. This varies, however,

depending on the individual system. For example, if a coating system has particularly poor dry or wet adhesion, is too thin compared to its permeability, is highly vulnerable to moisture penetration, or particularly poor in film quality, the system will ultimately fail. On highly polished bronze, good dry adhesion is more difficult to achieve, while mechanical adhesion and coating penetration into a porous patina may be helpful factors on a natural brochantite patina, at least for some period of time. However, these natural patinas are generally felt to be undesirable in appearance, and are often minimized by “gentle” blasting with a medium such as walnut shells. In the case of the blasted copper roof and patinated bronze samples, we may say that the weak links are the unstable substrates themselves. This is a warning to conservators that blasted or artificially patinated surfaces should be treated with special scrutiny and consideration, as well as, if possible, chemical analysis.

Conclusions and recommendations for individual coatings represented in this study are as follows. It is hoped that this study will encourage conservators to continue to explore coating options beyond waxing for outdoor bronzes.

The Wax Question

The purpose of this study was not to investigate the comparative effectiveness of different waxes for coating outdoor bronzes. Although there are reports that some waxes offer significantly better protection than others do,²⁴ only one representative wax was included in this study, the goal of which was to investigate currently viable coating options for outdoor bronzes. Waxes are without question the most commonly used types of protective coating on outdoor bronzes and brasses, as well as on other types of metal sculpture. This is in large part due to their ease of use, as well as to the common conception that waxes are “natural” and non-invasive. These ideas are, however, misconceptions in terms of outdoor metals in many situations. First of all, waxes significantly change the color and appearance of many objects by saturating existing patinas. After years of build-up, waxes may be extremely difficult if not impossible to completely remove. In addition, if a wax compromises an object’s protection in the outdoors, and allows corrosion to occur, this is extremely invasive to the aesthetic unity of an object as well as to its chemical stability.

On the other hand, an object with an existing, protective-type of patina, such as a coherent oxide or even a sulfate crust, may clearly benefit from the added protection of a wax coating. It is well known, in fact, that well-maintained wax coatings, i.e., renewed at least once per year, may reasonably protect a stable metal surface from obvious or disfiguring corrosion in the outdoors. Upon wax removal, however, it is commonly found that outdoor bronzes have significant oxide/sulfate layers that have been forming beneath the wax. As shown in this study, in the case of a metal surface that is highly prone to oxidation or acid-rain type corrosion, including highly polished and many artificially patinated surfaces, disfiguring pitting corrosion may occur under wax coatings. Unfortunately, because of the existence of many poor castings and other uncontrolled factors that commonly occur at the foundry level, many metal objects are highly vulnerable to corrosion in the outdoors. These types of surfaces are also vulnerable to more corrosion under a less protective coating.

A noteworthy result of this study is that walnut shell blasting of natural copper sulfate patinas, as commonly practiced in conservation treatments, was shown to have a

destabilizing effect on the substrate. This was evident from the significantly worse performance of coatings on the blasted vs. unblasted substrates, but in particular of the wax coating. In general, it may be said that due to the thinness of application, poor durability, and poor chemical resistance to acid rain solutions, wax coatings such as tested in this study cannot be considered to be in the same performance category as either acrylic lacquers or acrylic urethanes. This is clearly borne out by EIS results, in which the wax coating failed rapidly and irreversibly.

Nikolas Waterborne Acrylic Urethane

The waterborne acrylic urethane from G.J. Nikolas & Co. was chosen because it was developed specifically for copper alloys (although in indoor applications) and performed better than others of its type in previous work. It was hoped that creating a thicker, multi-layer coating layer than applied in Phase I could boost its performance. Waterborne coatings are of course highly sought for their safety and ease of use. Although the failure rating of this coating after accelerated weathering was markedly improved by adding a second brush coat of the polymer over the dried spray coat and a wax overcoat, especially on the polished bronze surface, the waterborne acrylic urethane remained a mediocre to poor performer overall. This coating performed particularly poorly over the unblasted, natural brochantite patina. This was ascribed in large part to the inability of the large polymer molecules to penetrate the natural mineral patina, as evidenced by lack of saturation of the light green patina and by thickness readings (see 1997 Final Report). Sitting virtually on top of the brochantite with very poor adhesion, the coating failed after only one year in natural outdoor weathering. One interesting result of this study is that the waterborne acrylic urethane performed best of the group on the artificially patinated bronze substrate, although still in mediocre ranking. This may be related to an increase in measured adhesion over the course of the weathering. No other explanation can be offered for this behavior without further study. In general, however, it appears that the properties of waterborne coatings studied in this project simply do not match the general performance of solvent-borne coatings at this point in time, although there are many commercial products in existence and they vary unpredictably from one to the next.

Incralac

Following wax, Incralac is without question the second most commonly used coating on outdoor bronzes worldwide. In this study, its performance was very mixed on the different substrates, i.e., fair to good on polished bronze, very good on 50-year-old copper roof, but poor on the blasted copper roof and artificially patinated bronze. The Incralac coating on polished bronze was shown to benefit in both Phase I and II from the addition of a wax topcoat. This topcoat appeared to be somewhat susceptible to whitening, however, and may need periodic renewal. These results appeared consistent for both accelerated and natural weathering, although the polished bronze sample exposed in the outdoors was lost in Phase II and Phase I results were relied upon. Removability tests of Incralac on the different substrates showed no evidence of crosslinking or other changes in coating solubility with weathering. Adhesion testing of Incralac on the four substrates showed significant loss of adhesion on the polished and patinated bronze surfaces after accelerated and natural weathering, but not on the copper

roof substrates. ATR investigation of the polymer/metal interface showed that de-adhesion is largely corrosion-induced. In addition, EIS results for Incralac on polished bronze predict catastrophic loss of resistance to moisture after some period of cycling. In this light, it is reasonable to assume that Incralac can perform well for only a limited period of time, given careful surface preparation and application. The latter is not a minor point, since application of the lacquer evenly, without resulting orange peel, takes much practice.

BTA + BASF Acrylic Urethane + Wax

For all but the artificially patinated bronze substrate, this coating performed reasonably well. EIS predictions show that the coating is extraordinarily resistant to moisture and salt penetration. Adhesion problems to metal must be overcome in its use, however, and this may have been the source of a lower overall failure rating after accelerated weathering on the polished bronze. The coating performed remarkably well on the blasted copper roof substrate, as well as on the unblasted copper roof. In these cases, penetration into the natural patina to form a matrix appeared good, but resulted in color saturation of the patina, although it effectively prohibited moisture ingress. The uneven success of this coating reported in the field may well be related to surface preparation, which must be scrupulous to achieve reasonable adhesion. Because this coating is crosslinked, it must be removed by mechanical methods.

Nikolas Acrylic/Acrylic Urethane/Wax

This 3-part coating system was put together as a model system in the Phase I testing. The main purpose of the acrylic underlayer is to allow a method for solvent removal of the coating, since it was shown in the laboratory that the top layer was sufficiently permeable to organic solvents to allow swelling of the acrylic, followed by peeling of the entire coating after exposure to toluene or acetone (see 1997 Final Report). The acrylic underlayer also has the advantage of good adhesive properties to the metal. The purpose of the acrylic urethane as a main or second coat was to provide the added protection and durability of the crosslinked coating. This appeared, in fact, to work. The wax topcoat was added mainly to matte the shiny appearance. As stated, the final coating system in Phase II was slightly thicker than intended and may have had a small boost in performance from this advantage, especially with regard to EIS results. The very good performance of this coating on polished bronze and the 50-year-old copper roof brochantite patina (unblasted) suggest that this coating system is a good candidate for experimentation in the field, especially in cases where a low-maintenance, high performance coating is needed.

Recommendations for Future Work

Material products of Phases II and III include three additional sets of model samples, either without weathering (controls), after accelerated weathering, or after natural, outdoor weathering, totaling 122 samples. Products also include digital images of the samples and a software program script for their evaluation using Scanalytics IPLab

software. It is recommended and hoped that these products of the study be put to use for further study, including monitoring of the progress of samples that continue to undergo natural weathered (Phase II, set C) on the roof of the Natural Gallery of Art. Additional EIS of the copper roof samples would be especially valuable, as well as more extensive ATR investigation of the polymer/metal interface chemistry with weathering. Future plans for related work include testing of a single coating with varying CuBTA underlayer film thickness by EIS in order to test hypotheses formed in this study. Further EIS work may also include comparison of these results to wax coatings reported to perform well in other studies. Field studies of the Nikolas acrylic/acrylic urethane and BASF acrylic urethane systems are highly recommended, as is experimentation in general methods of coating removal. Finally, testing of other new coatings developed and/or adapted specifically for application on outdoor bronzes remains a wide open field in which many contributions are possible.

Publications and Presentations:

L. Brostoff and B. René de la Rie, "Final Report to the NCPTT 1996 Grant Program: Research into Protective Coating Systems for Outdoor Bronze Sculpture and Ornamentation. Phase I."

L. Brostoff, T. Shedlosky, and B. René de la Rie, "Final Report to the NCPTT 1997 Grant Program: Research into Protective Coating Systems for Outdoor Bronze Sculpture and Ornamentation Phase II."

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Lynn B. Brostoff and E. René de la Pie, "Chemical Characterization of Metal/Coating Interfaces from Model Samples for Outdoor Bronzes by Reflection-Absorption Infrared Spectroscopy (RAIR) and Attenuated Total Reflection Spectroscopy (ATR)" in Mourey, W. et al., ed., Metal 98 Proceedings, of the International Conference on Metals Conservation, ICOM CC Metals Working Group, May 26-29, 1998, Draguignan, France (James & James, London), pp. 320-328.

Lynn B. Brostoff, Tara Shedlosky, and E. René de la Rie, "External Reflection Study of Copper-Benzotriazole (Cu-BTA) Films on Bronze in the Context of BTA Pretreatments for Coated Outdoor Bronzes" presentation and paper in press, IIC2000 Congress, Melbourne, Australia, October 10-14, 2000 (Appendix A).

Tara Shedlosky and Lynn B. Brostoff. “The Application of Digital Image Analysis to Performance Assessment of Coatings for Outdoor Bronze and Copper,” presentation at AIC2000 Conference, Philadelphia, Pa., June 8-13, 2000 (Appendix B).

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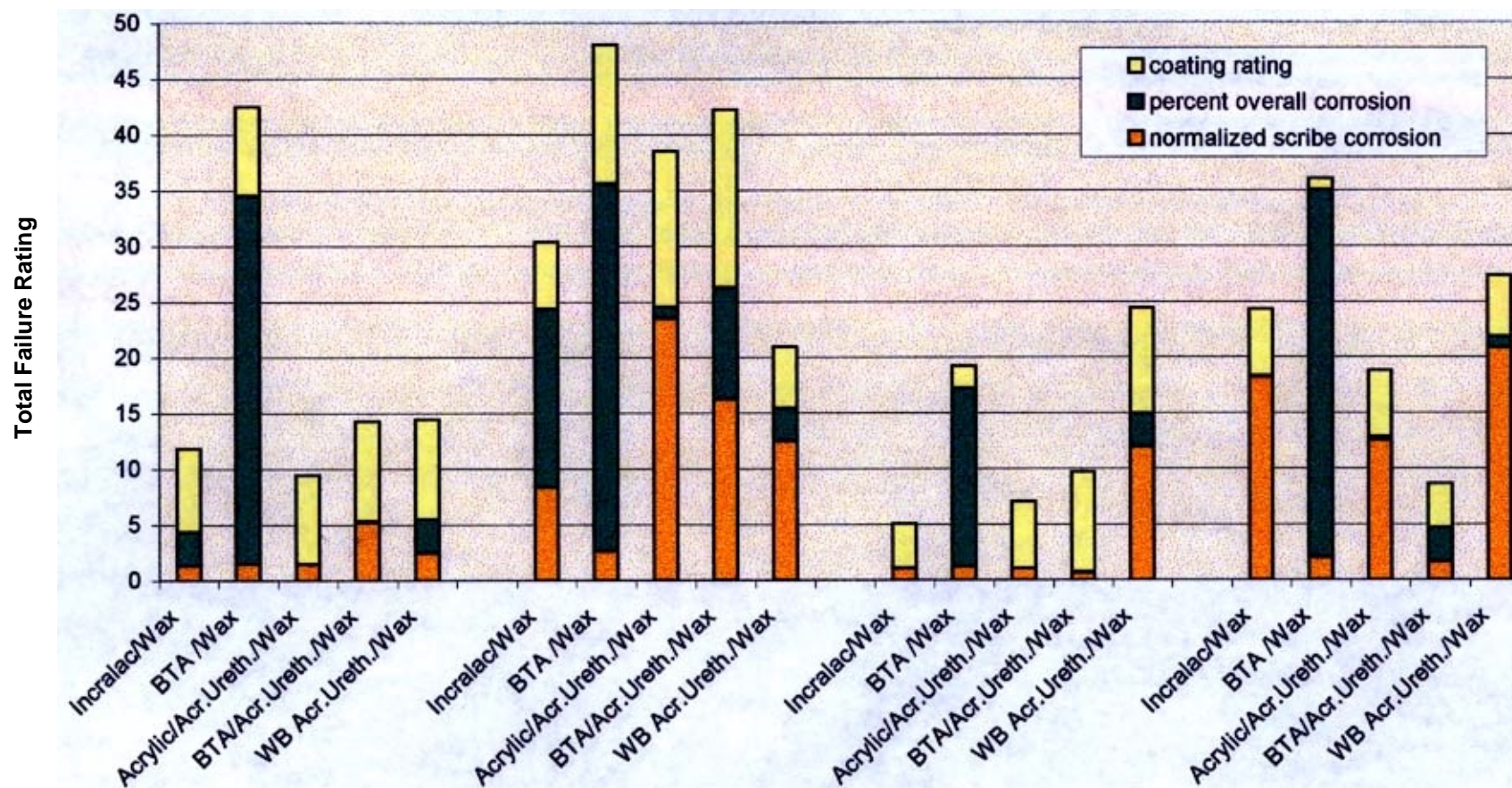
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Table I
Descriptions of Coated Bronze and Copper Samples after Natural, Outdoor Weathering, Phase II

Sample	Polished, Cast Bronze		Patinated, Cast Bronze		50-yr.-old Copper Roof		Walnut shell-blasted, 50-yr.-old Copper Roof	
Corrosion Area	surface	scribe	surface	scribe	surface	scribe	surface	scribe
1- Inralac + wax			Tiny blisters overall.	A very small amount of green corrosion in scribe mark. More marked overall corrosion.	Light orange peel.	No visible change.	Small amount of light green corrosion.	Light peeling around scribe mark.
2- BTA + wax			Matte surface and patina change to irregular and mottled appearance.	No visible change.	white haze overall. Dark and matte;	No visible change.	Some water spotting. Darkened and matte.	No visible change.
3- NK acrylic urethane + wax			Tiny blisters in the coating. Shiny surface; worn wax layer.	Peeling around scribe mark (pulling up both the patina layer and the coating).	No visible change.	Very small amount of corrosion within scribe mark.	Slight darkening.	Slight peeling. Light green corrosion within scribe mark.
4- BTA + BASF acrylic urethane + wax	No visible change.	Very small amount of bright green corrosion within scribe mark.	Small white blisters overall,	Very small amount of green corrosion within scribe mark.	Bluish green surface coloring. Whitened appearance in coating,	visible change.	No visible changes.	Green corrosion within scribe mark. Peeling around the edges of scribe mark.
5- NK waterborne acrylic urethane + wax	Tiny pox marks overall.	Green powdery corrosion within scribe mark.	Blisters overall. A few small green corrosion spots,	Small amount of green corrosion within scribe mark.	Yellowed. Severe peeling. Light green corrosion in the exposed areas	Peeling around scribe mark. Very small amount of light green corrosion	Slightly darkened patches overall and whitened appearance to coating.	Slight peeling at scribe mark.
6-No coating	Patina even, smooth, matte, and purple-brown color. A few green corrosion spots seen under magnification.	N/A	Patina change to mottled orange, light and dark brown coloration	N/A	Slight darkening.	N/A	A few light green Corrosion spots. Slight darkening overall.	N/A

Figure 1

Total Failure Ratings for Coatings on Bronze or Copper Substrates After 120 Days Accelerated Weathering



I. Polished, Cast Bronze

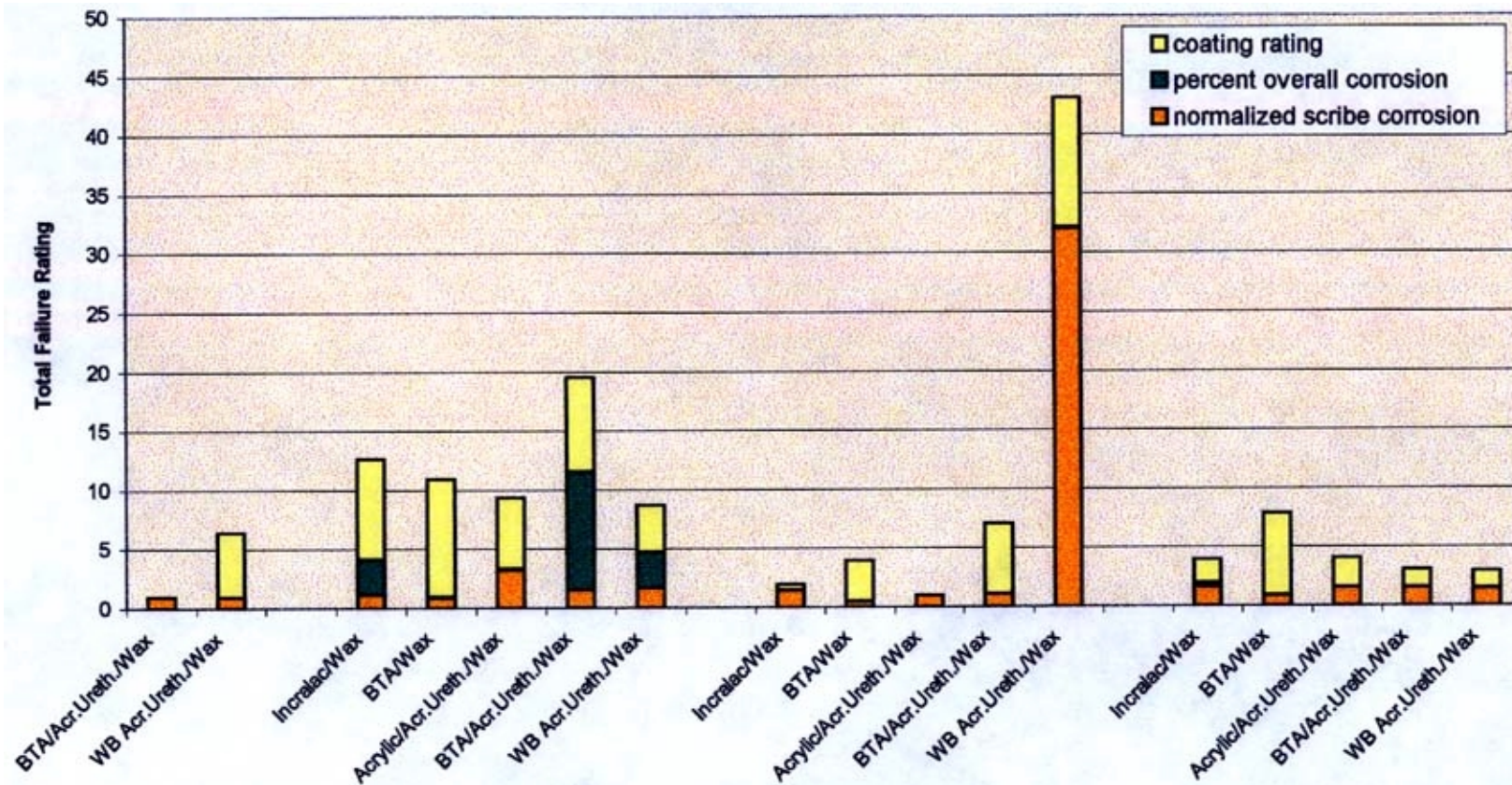
II. Patinated, Cast Bronze

III. 50-yr-old Cu Roof

IV. Blasted Cu Roof

Figure 2

**Total Failure Ratings for Coatings on Bronze or Copper Substrates
After Approx. 1 Year Natural Weathering**



I. Polished, Cast
Bronze

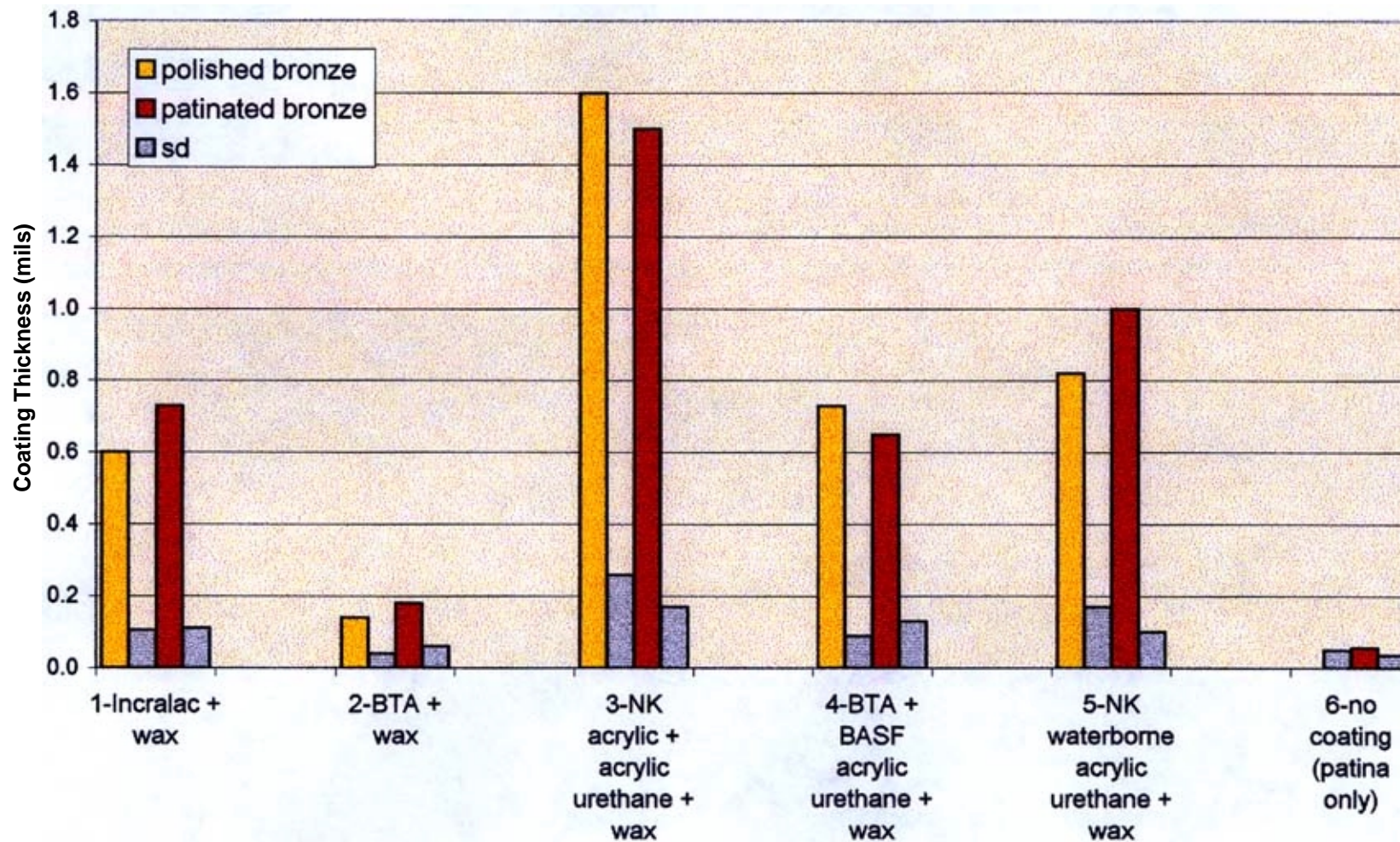
II. Patinated, Cast
Bronze

III. 50-yr-old Cu Roof

IV. Blasted Cu Roof

Figure 3

**Coating + Patina Thickness and Standard Deviation (sd)
on Unweathered Bronze Substrates, Phase II**



Sample

Figure 4

**Coating + Patina Thickness and Standard Deviation (sd)
on Unweathered 50-year-old Copper Roof Substrates, Phase II**

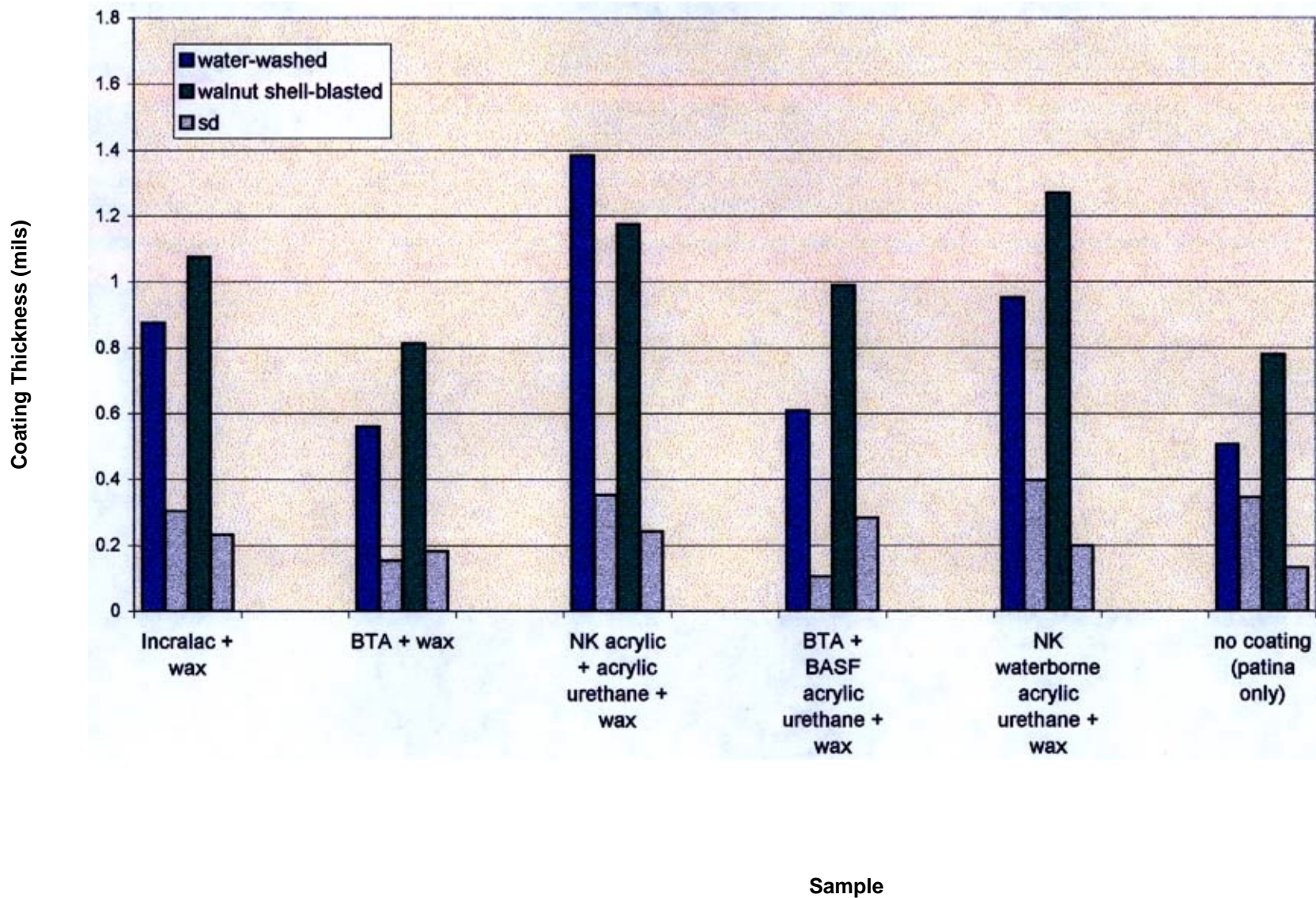
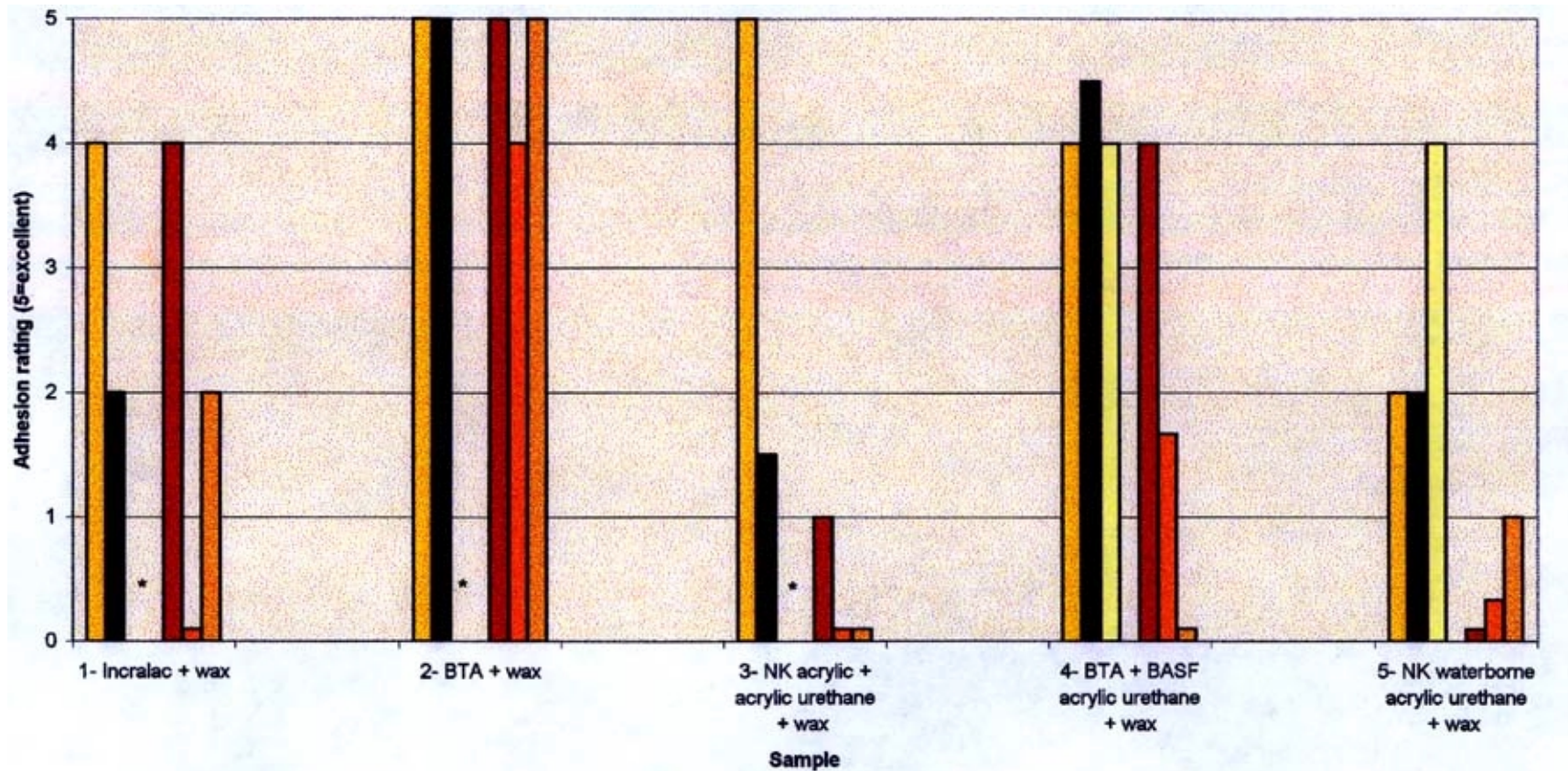


Figure 5

Cross-Cut Adhesion Rating of Coatings on Cast Bronze, Phase II Before and After Accelerated and Natural Weathering



*Note that the first three naturally weathered samples are missing, and the adhesion is not reported.

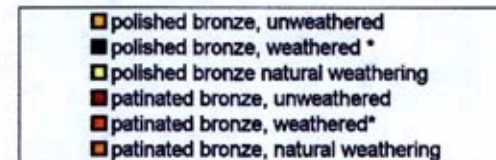


Figure 6

**X-Cut Adhesion Ratings of Coatings on \$0-Year Old Copper Roof, Phase II,
Before and After Accelerated Weathering**

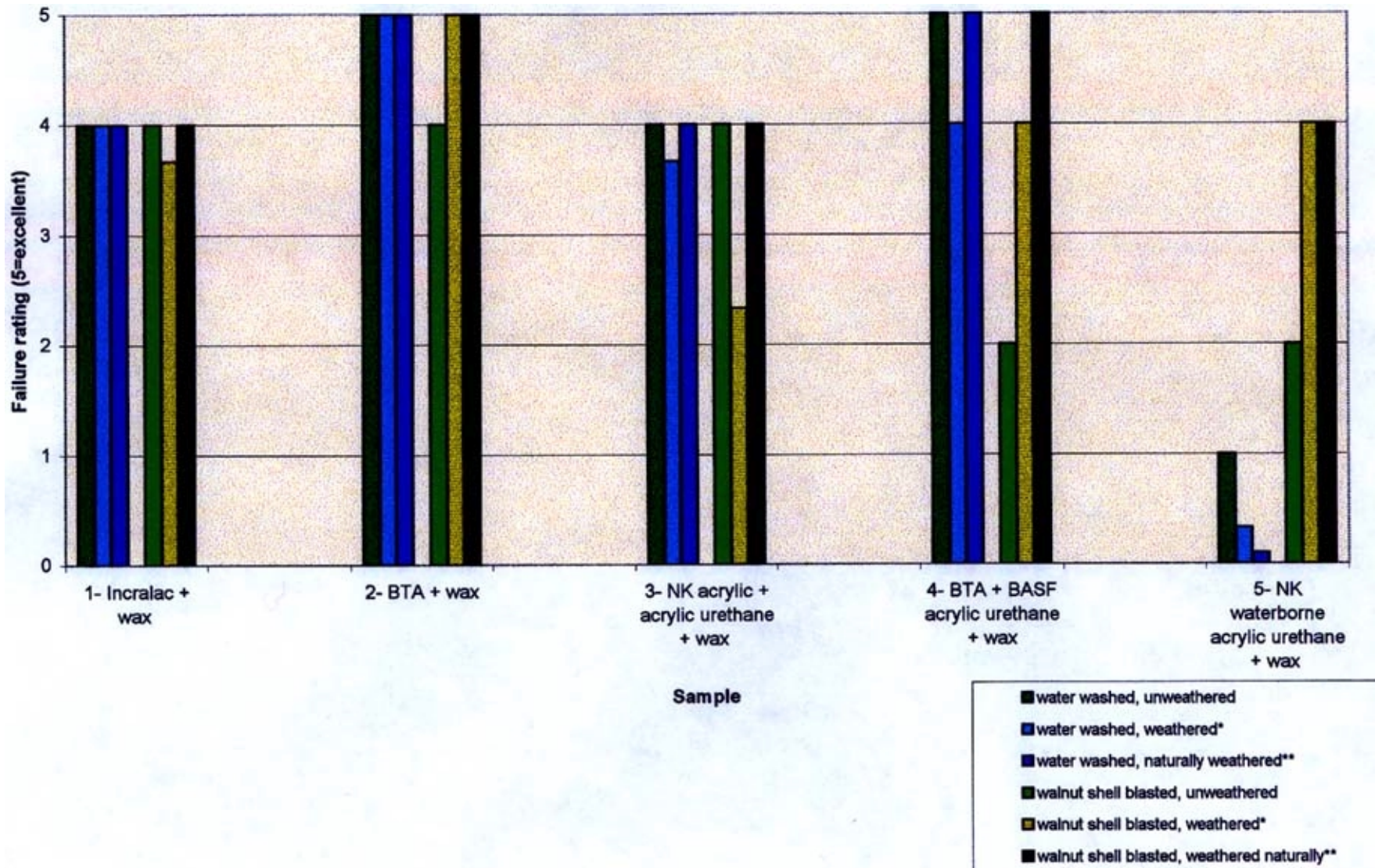


Figure 7

**ATR spectrum of Carbonyl Absorbance in Incralac Films on Polished Bronze,
A) With and B) Without Accelerated Weathering**

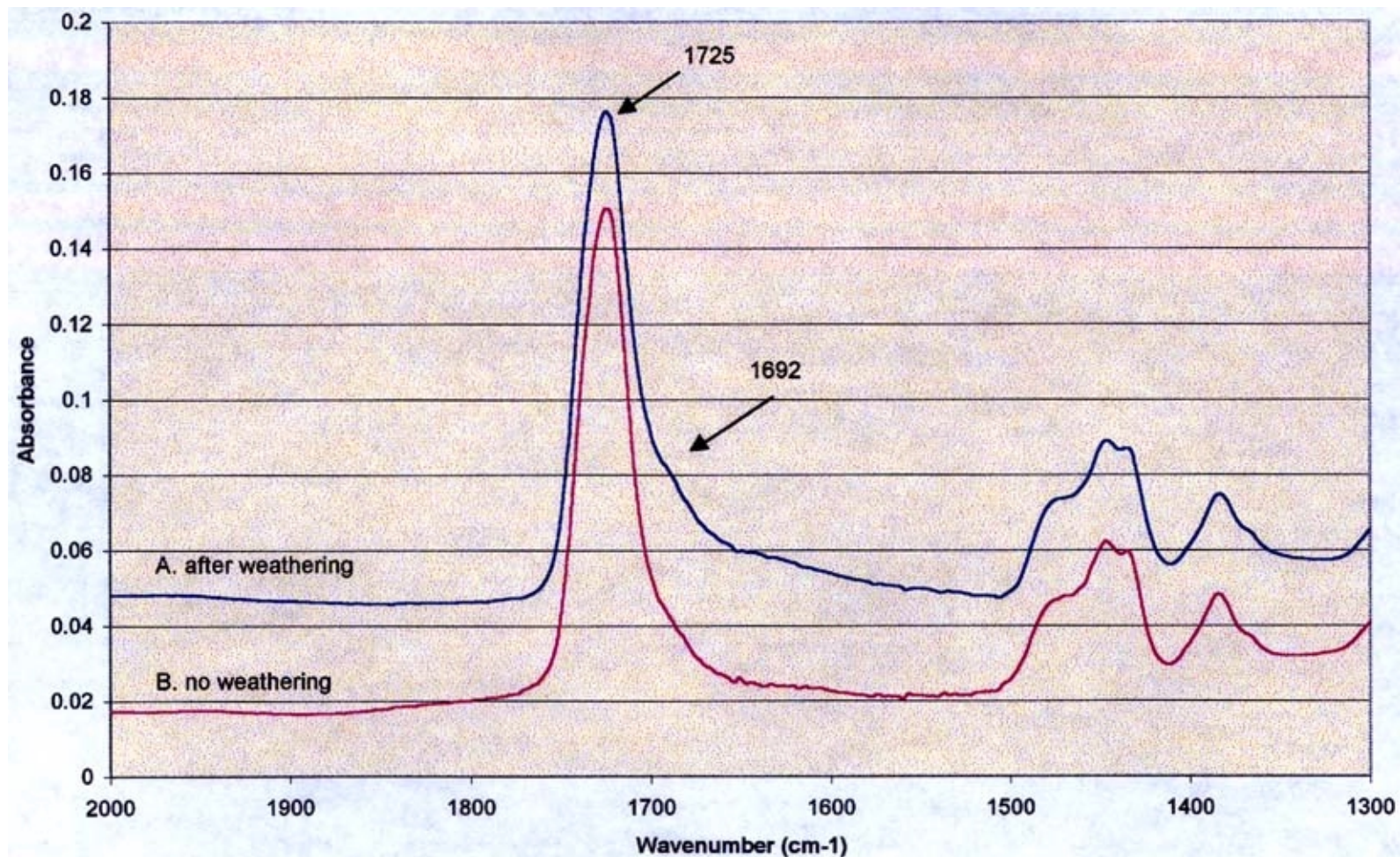


Figure 8
Bode Plots of Polished Bronze Plates
During Prohesion[®] and QTJV[®] Cycling

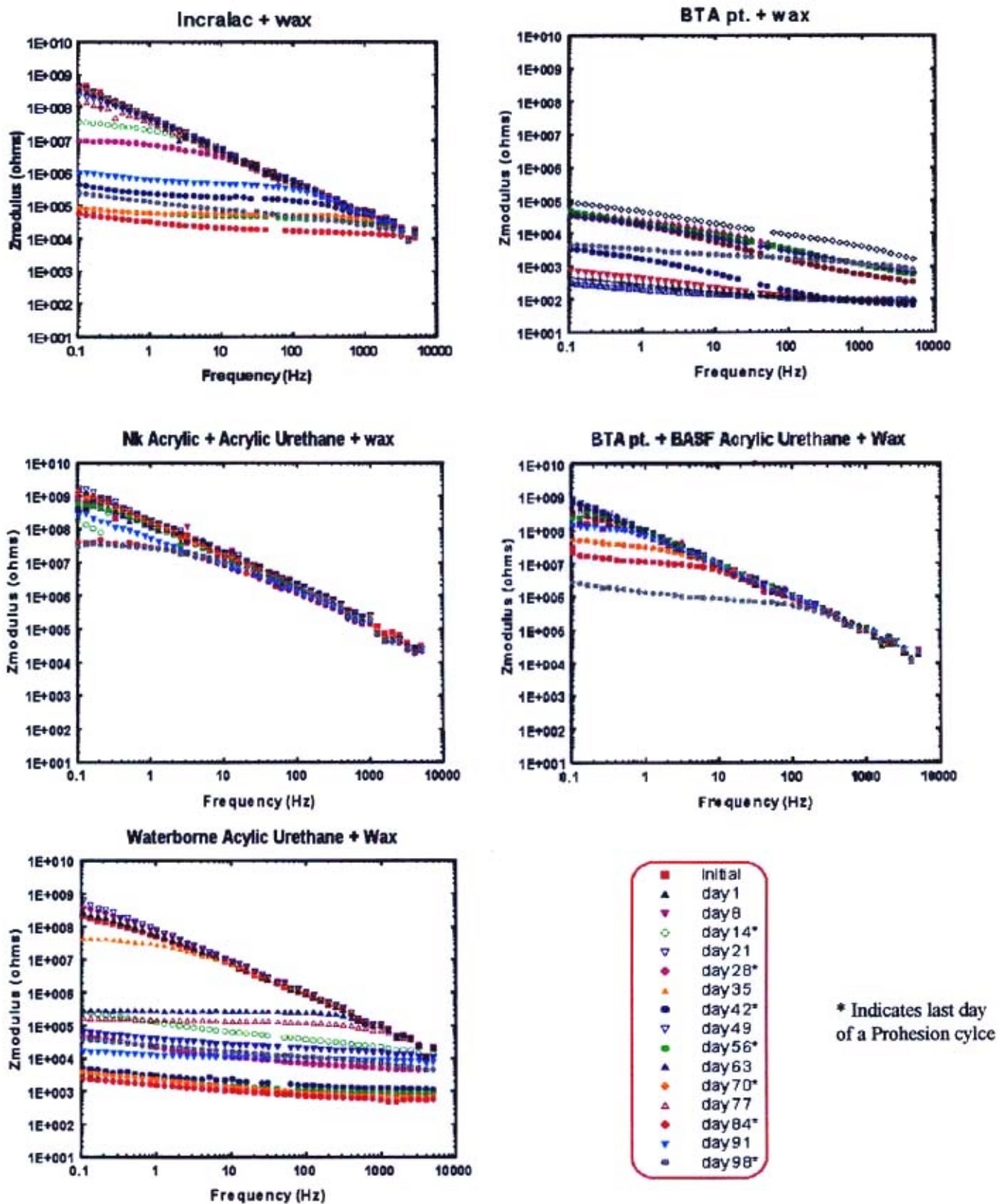


Figure 9

**National Gallery of Art Accelerated
Weathered Samples**

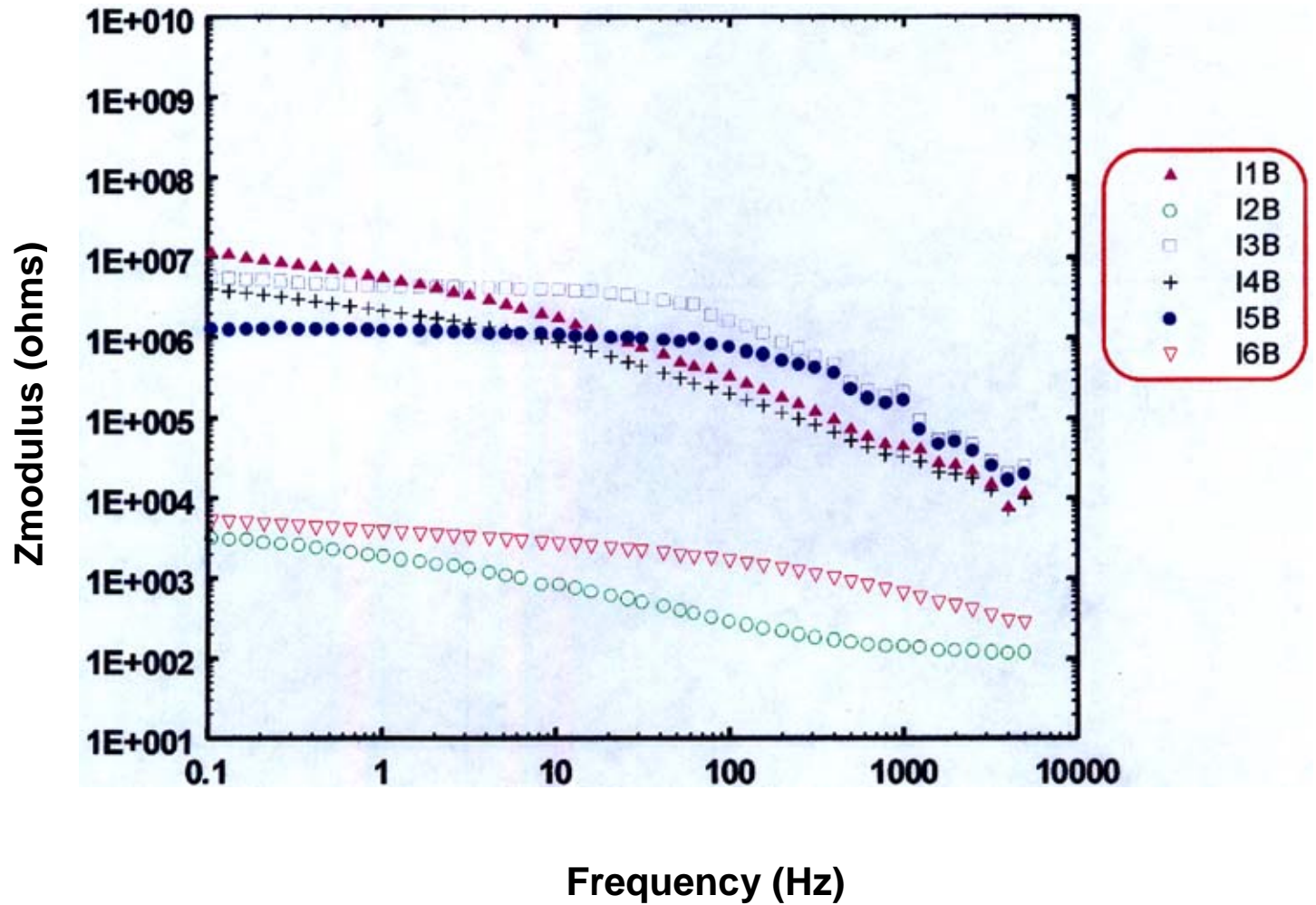
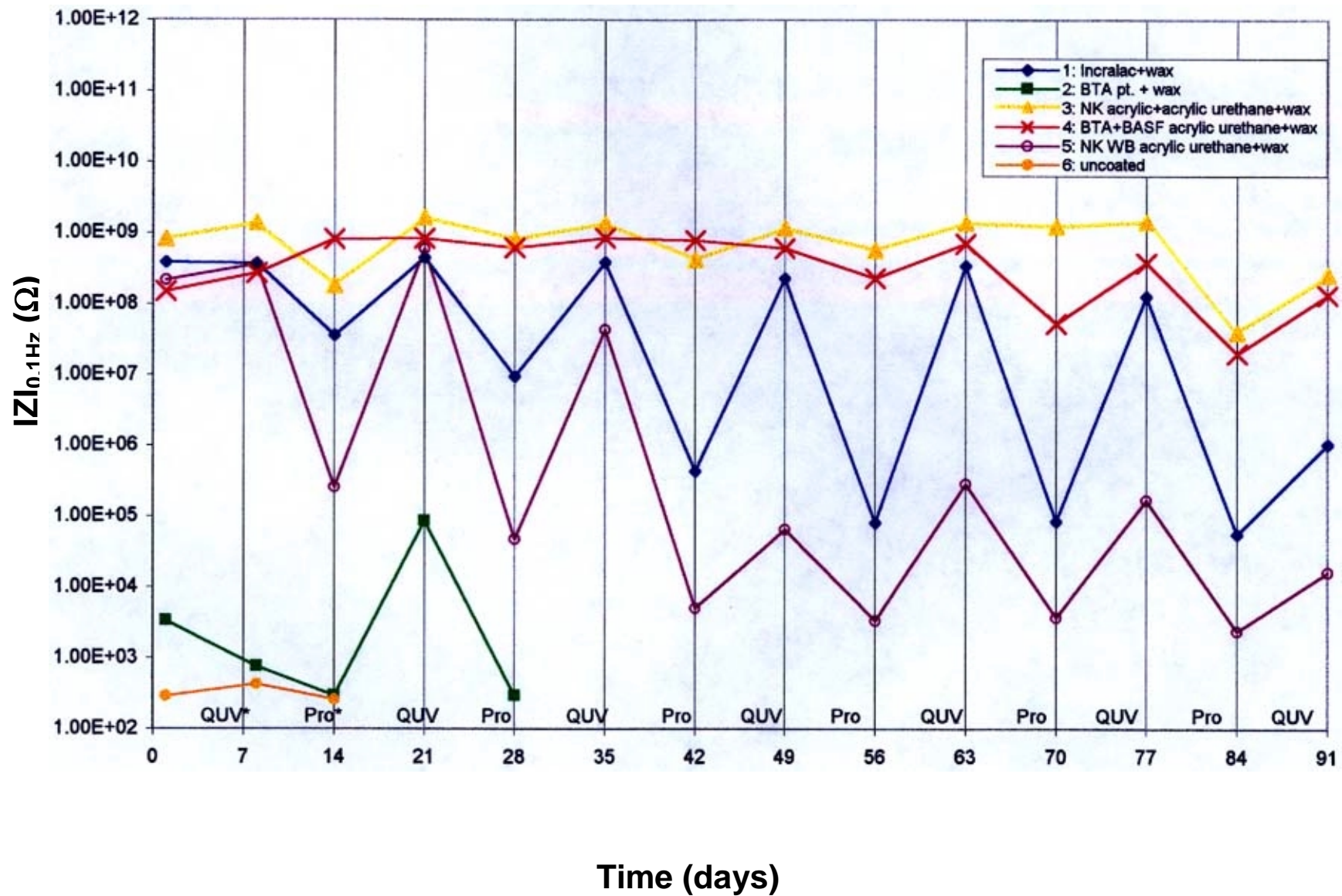
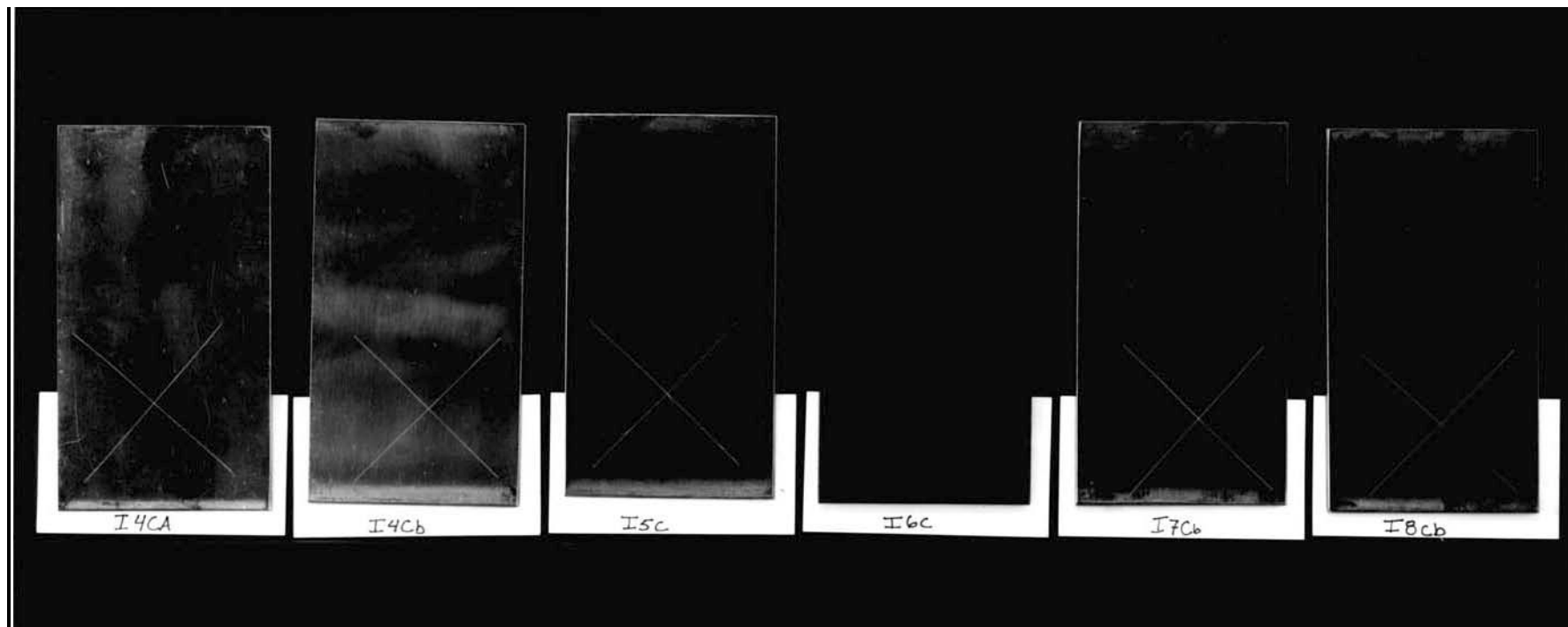


Figure 10

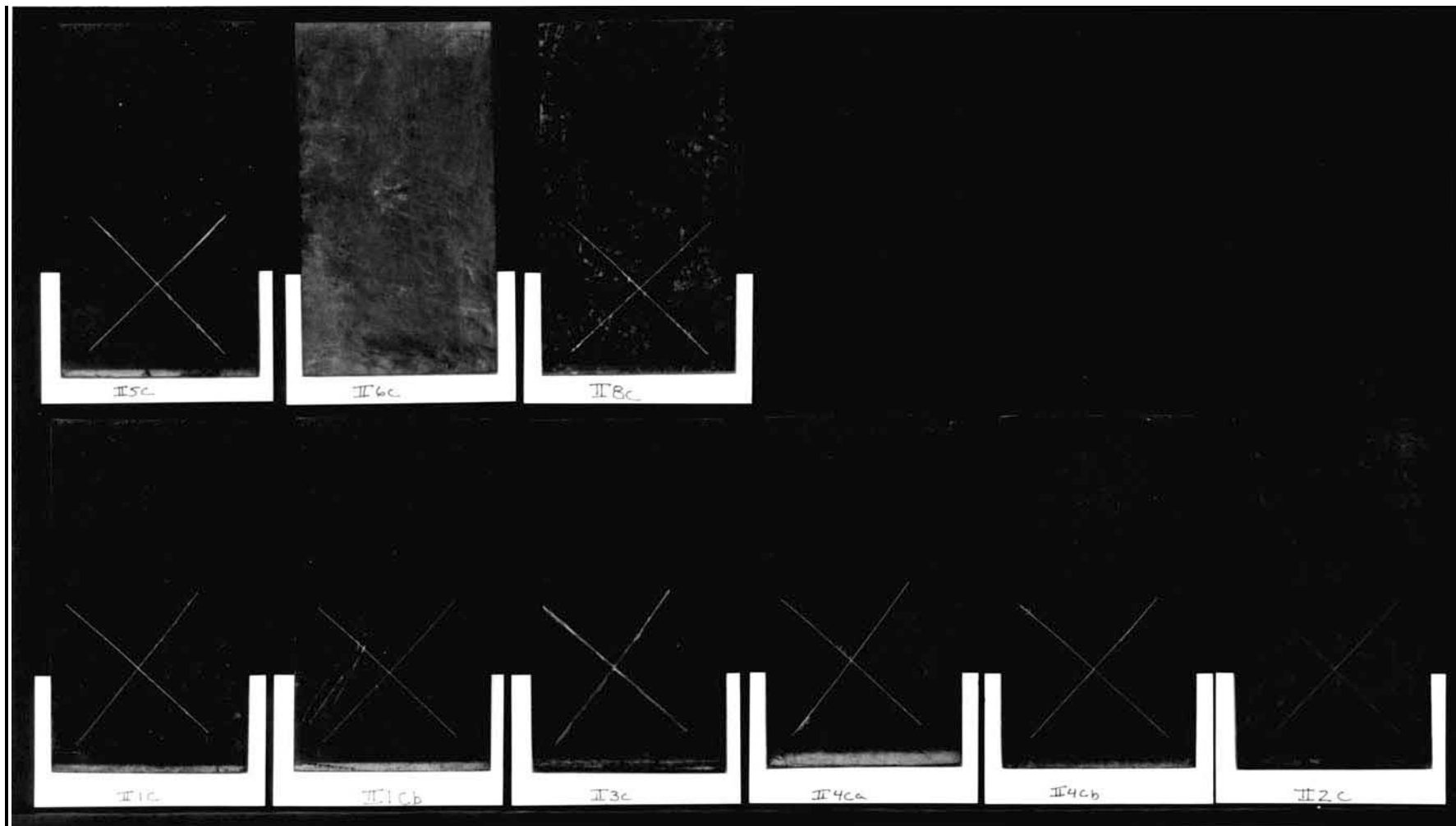
**$|Z|_{0.1\text{Hz}}$ vs. Time of QUV/Prohesion Exposure
for Coatings on Polished Bronze Samples**





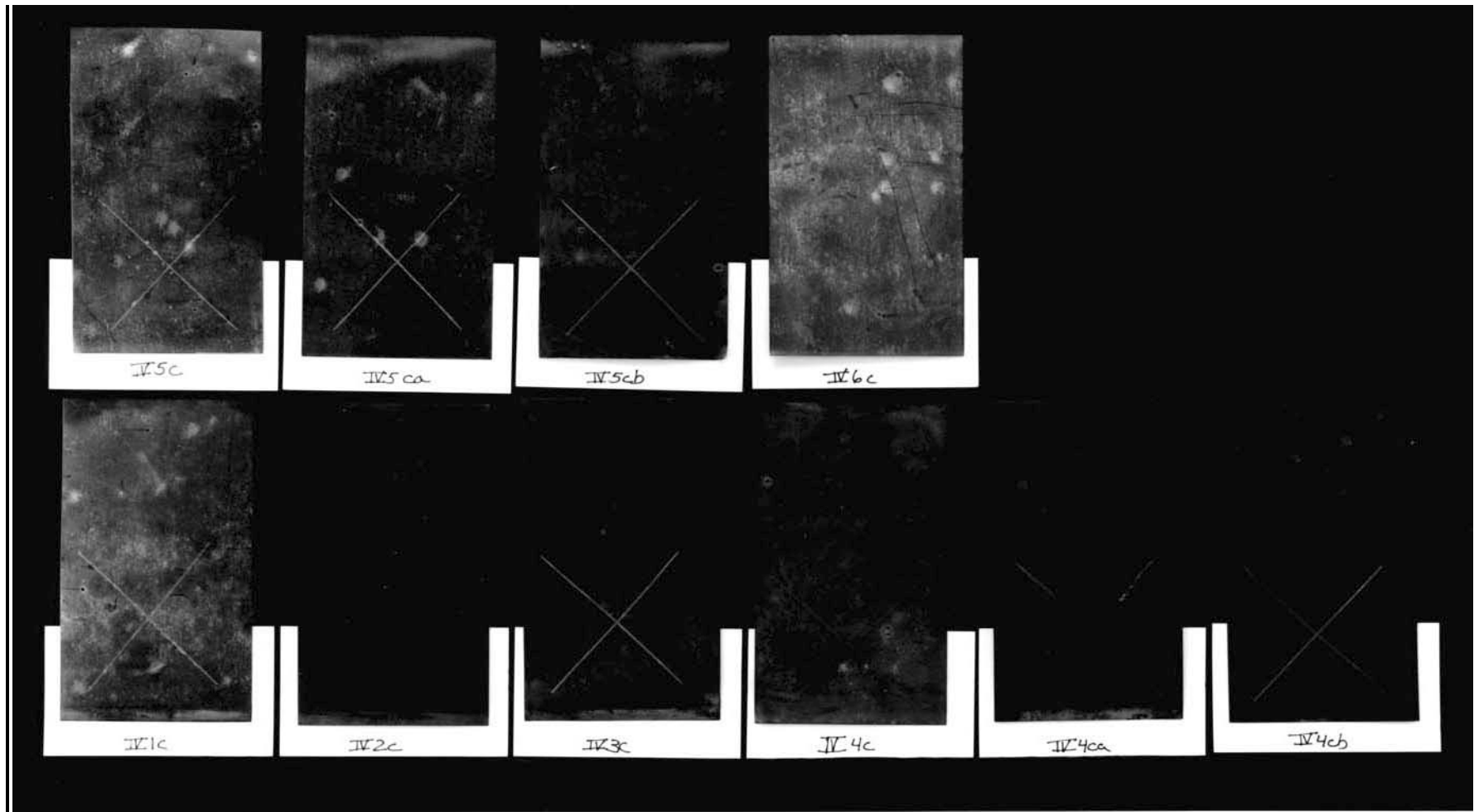
NATURALLY WEATHERED Polished
Bronze samples. After 1 year outside.

- 14 = BTA + B ASF acrylic urethane + wax
- 15 = waterborne acrylic urethane + wax
- 16 = no coating
- 17 = BASF acrylic urethane
- 18 = waterborne acrylic urethane



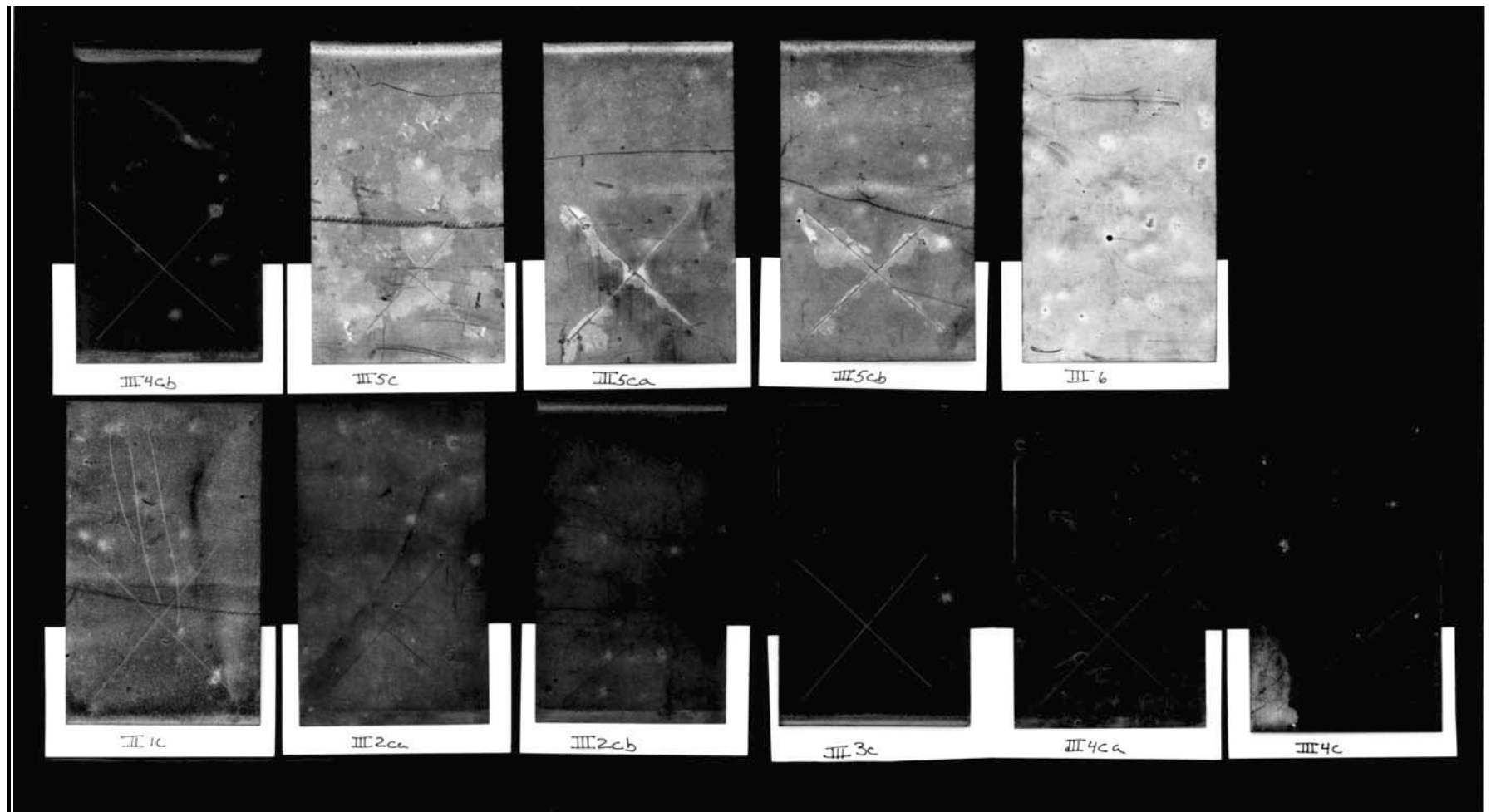
NATURALLY WEATHERED Artificially
Patinated Bronze. 1 year Outdoor Weathering.

- 1 = Inralac + wax
- 2 = BTA + wax
- 3 = NK acrylic + acrylic urethane + wax
- 4 = BASF + BASF acrylic urethane + wax
- 5 = waterborne acrylic urethane + wax
- 6 = no coating
- 8 = waterborne acrylic urethane



NATURALLY WEATHERED Walnut-shell
Blaster Copper Roof Samples. After 1 year outside.

- 1 = Inralac + wax
- 2 = BTA + wax
- 3 = NK acrylic + acrylic urethane + wax
- 4 = BASF + BASF acrylic urethane + wax
- 5 = waterborne acrylic urethane + wax
- 6 = no coating
- 8 = waterborne acrylic urethane



NATURALLY WEATHERED Water-washed
Copper Roof Samples. After 1 year outside.

- 1 = Inralac + wax
- 2 = BTA + wax
- 3 = NK acrylic + acrylic urethane + wax
- 4 = BASF + BASF acrylic urethane + wax
- 5 = waterborne acrylic urethane + wax
- 6 = no coating
- 8 = waterborne acrylic urethane

Appendix A

EXTERNAL REFLECTION STUDY OF COPPER-BENZOTRIAZOLE FILMS ON BRONZE IN RELATION TO PRETREATMENTS OF COATED OUTDOOR BRONZES

Lynn B. Brostoff, Tara J. Shedlosky, and E. René de la Rie.

ABSTRACT

Copper-benzotriazole (CuBTA) film growth on rolled bronze was investigated by external reflection, also known as reflection-absorption infrared spectroscopy. Results confirm that the film growth in near-neutral conditions is time and concentration or solvent dependent. New evidence was obtained for step-wise, linear development of these Cu(I)BTA films. Ellipsometric measurements of the thickness of representative Cu(I)BTA films revealed a range of 100-450 Å for immersions up to 1 week. Electrochemical impedance of several Cu(I)BTA films formed at different immersion times was measured. Some properties of the Cu(I)BTA films, including heat stability, oxidative stability, and ability to form on unclean surfaces or under the coating Incralac®, were also investigated. These results, viewed within the context of accelerated indoor and natural outdoor weathering of coated bronze and copper samples, also provide a rationale for the limited efficacy of BTA pretreatments often observed on outdoor bronzes. The protection afforded by thin films of CuBTA as normally applied in conservation pretreatments appears to be insignificant compared to protection afforded by much thicker, polymeric coatings used in harsh outdoor environments.

INTRODUCTION

Benzotriazole (BTA) has been in use as a corrosion inhibitor for the conservation treatment of bronzes since the late 1960s [1], and despite the search for improved inhibitors, 1H-benzotriazole (BTAH) remains one of the most effective and acceptable

anti-corrosion treatments available for copper alloys today [2]. Recent articles and lectures have asserted that BTA is safe for use in conservation [3], and conservators in the fields of archaeological and outdoor sculpture conservation continue to rely on BTA for treatment of archaeological as well as outdoor copper alloys and bronze art and ornamentation. However, the uneven success of this agent in treatments for bronze disease and in prevention of bronze corrosion in outdoor exposures remain important subjects of scrutiny and scientific research. In particular, a scientific basis for the choice of treatment parameters has been lacking.

The majority of investigations into the inhibition effect of BTAH on copper and copper alloys advance the theory that CuBTA films protect the metal from corrosion by means of a highly impermeable physical barrier layer to chloride and sulfate ions, rather than by chemical or electrochemical means. Film formation under non-corrosive conditions has been found to be self-limiting, leveling off as the thickness effectively reinforces the underlying oxide and blocks the metal surface [4-6]. Under acidic conditions, i.e., $\text{pH} \leq 4.0$, the underlying oxide or patina tends to dissolve and be replaced by thick CuBTA films, reported to grow up to 5000 Å. Under these conditions, CuBTA film formation is accompanied by simultaneous corrosion beneath the CuBTA film, so that the combined processes result in nearly unlimited growth [4,7]. However, these CuBTA films are known to be much less protective [4-6].

In this light, CuBTA inhibition is shown to be highly dependent on thickness, but also on properties such as porosity and degree of polymerization. Investigations into the dependence of CuBTA thickness on BTAH concentration and exposure time are not unanimous and have typically examined copper maintained in BTAH solutions at

concentrations much lower than used in conservation applications [5,8]. Optimization of these film properties for conservation applications, as well as an understanding of corresponding chemical and physical structure, and are thus of key importance in the field and have remained a subject of speculation and trial and error.

In the context of a broader study into new coatings for outdoor bronzes at the National Gallery of Art [9-11], the role of CuBTA films under thicker protective coatings was probed. In this study, a series of cast bronze and 50-year-old, naturally corroded copper samples a) underwent various surface preparations, including brush-coating with 1.5% BTAH/ethanol, b) were given various protective coatings, and c) were exposed to both accelerated indoor and natural outdoor weathering. Visual inspection and x-ray diffraction measurements of corrosion on uncoated substrates treated with BTAH showed this treatment by itself has little inhibiting effect on the formation of chlorides and black corrosion in accelerated and natural weathering. Furthermore, BTAH treatment prior to the application of a coating did not show any clear performance benefit in our testing regimes. These observations are supported by reports in the literature that air-dried Cu(I)BTA films have vastly decreased corrosion protection in NaCl solutions compared to films that form and remain in a NaCl/BTAH solution [6,12]. It is also known that CuBTA protection in sulfate solutions is superior to that in chloride solutions [13]. It is thus unclear whether it is possible to optimize BTA pretreatment of outdoor bronzes and, in so doing, unambiguously boost the protection of a coating system.

In order to gain a better understanding of these observations, CuBTA film formation on rolled bronze was studied by external reflection, also known as reflection-absorption infrared spectroscopy (RAIR). RAIR was used to investigate the thickness of

CuBTA films formed on rolled bronze in various conditions, as well as to gather chemical information about the films themselves. The formation of a CuBTA film underneath organic coatings such as Incralac®, which contains BTAH, was also investigated. Chemical aspects of the films will only be summarily discussed in this paper and will be elaborated in a future publication. Ellipsometry and electrochemical impedance spectroscopy (EIS) were also utilized to confirm trends observed by RAIR.

EXPERIMENTAL

RAIR of thin Cu(I)BTA films formed on rolled bronze by immersion in a) 1.5 wt.% BTAH/ethanol, b) 3.0 wt.% BTAH/ethanol, or c) 1.5 wt.% BTAH/water was performed with a Bio-Rad Digilab FTS-60A Fourier transform infrared spectrometer fitted with a Harrick versatile reflection attachment for center-focused beam and a retro-mirror accessory, plus a wire-grid polarizer set for parallel beam polarization. The angle of incidence in all cases was 78 degrees. Samples were purged with dry air for 10-20 minutes to minimize the presence of atmospheric moisture. The final reflection spectra were obtained by digitally subtracting that of the cleaned bronze sample taken before immersion in the BTAH solution and placed with the same geometry in the accessory before and after treatment. In some cases of very long immersion in BTAH solutions, sample spectra were produced by subtracting that of a new, freshly scanned, untreated rolled bronze coupon. Absorbance at 745 cm^{-1} was calculated by the WIN-IR software from the maximum height of this peak to a baseline drawn between 835 to 729 cm^{-1} .

Solutions of BTAH (Aldrich, 99%) were made with HPLC-grade ethanol or millipore, distilled and deionized water. The pH of aqueous BTAH solutions was 5.30.

The rolled bronze (Lubaloy Co.) was spring-tempered, 425 bronze, 0.016 gauge, with an alloy composition of 88.5% Cu, 9.5% Zn, 2% Tin. Rolled bronze samples were polished with a series of Micro-mesh cloths from either 2400 or 6000, to 12000 mesh. The polished samples were solvent cleaned by wiping and rinsing with alternating polar and non-polar solvents until they passed the water-break test², immersed into the appropriate BTAH solution, rinsed thoroughly with ethanol, and air dried.

Ellipsometry was performed with a Rudolph Research Inc. thin film ellipsometer, type 43603-200E. Film thickness was calculated from measurements of the delta and psi parameters using a film refractive index of 1.6 [5,14]. An uncoated bronze coupon served as the background, so that the thickness of the natural cuprous oxide layer was subtracted from CuBTA thickness measurements.

EIS was conducted at North Dakota State University on a set of polished rolled bronze samples that had been immersed in 3% BTA/ethanol solutions for 4 minutes, 1046 minutes, or 10,047 minutes. EIS measurements were taken with a Gamry Instruments PC-3 Potentiostat, using a removable 1.5 inch (outer diameter) glass tube clamped to the bronze coupon by an O-ring. The glass tube was filled with the dilute Harrison's solution (0.35 wt. % $(\text{NH}_4)_2\text{SO}_4$ and 0.05 wt. % NaCl in H_2O). A saturated calomel reference electrode and a platinum counter electrode were also immersed in the solution. The amplitude applied to the system was 5 mV, and the frequency range was from 0.1 Hz to 10,000 Hz. Impedance modulus is reported as an average of three spots on each sample.

RESULTS AND DISCUSSION

RAIR

Figure 1 shows a typical RAIR spectrum of CuBTA as produced in this experiment. Despite the very low absorbance scale here, RAIR is shown to be sensitive enough to clearly exhibit the cuprous complex, Cu(I)BTA, as formed on the naturally oxidized, rolled bronze coupon. The most intense absorption peak in the spectrum near 745 cm^{-1} arises from the in-phase, out-of-plane, 4 adjacent hydrogen wag aromatic vibration, which is unaffected by complexing³. This spectrum is in excellent agreement with the transmission spectrum of CuBTA in a KI pellet, as well as the reflectance spectrum of a CuBTA film on copper formed in a BTAH/NaCl solution at pH 3.0, as published by Poling [5]. These spectra are distinct from typical spectra of uncomplexed BTAH. As similarly noted by Poling, reflectance spectra of the CuBTA films in our study showed little differences regardless of formation conditions, except as noted below. Further discussion of the chemical nature of the CuBTA films as shown by RAIR will be the subject of a future publication.

The Beer-Lambert law states that absorbance intensity is the product of absorbtivity, sample thickness and concentration. As shown by Greenlar [16], for external reflection at a glancing angle on a perfectly reflecting surface, the percent reflectance of the sample vs. that of the uncoated substrate is approximately proportional to percent transmittance of a transparent sample. Since absorbtivity of sample films is constant in this experiment, and assuming, for the present, that density in the films is constant, absorbance at 745 cm^{-1} may be used to track the film thickness over different immersion times in one of three BTAH solutions. Although the relationship between

absorbance and film thickness is expected to show some deviation from linearity above about 100 Å, the relationship generally holds up to 1000 Å film thickness.

Figure 2 shows absorbance at 745 cm^{-1} vs. time of immersion for rolled bronze coupons dipped in various BTAH solutions. The trendlines are best fit linear equations, although they appear curved from plotting time on a logarithmic scale. Allowing for scatter in the data, trendlines indicate that thickness of CuBTA films generally increases linearly with time of immersion, and furthermore that rates of increase differ in the three solutions. The scatter is most likely due to the large amount of samples run in this series over a very long period of time, which may have introduced some variability in the sample preparation and in the substrates themselves. It should be noted, however, that data trendlines show improved fit overall with 2nd order polynomials, suggesting that reaction kinetics are complex, as discussed below.

In particular, this plot indicates that within experimental error change in thickness of CuBTA films in all solutions is quite small during the first 90 minutes or so. By one day of immersion, however, a strong divergence of the growth rate in 3% BTAH/ethanol is obvious. This indicates that the growth rates of CuBTA films increase with effective concentration of BTAH in solution. Although there are likely to be additional solvent effects in the aqueous solution, such as pH, it is reasonable to expect decreased activity of BTAH in water due to its polar and slightly acidic nature.

Film Thickness

Ellipsometry of selected samples immersed in BTAH solutions from 4 minutes to 1 week indicated that the CuBTA films ranged in thickness from about 100 to 450 Å

(Figure 3). Within experimental error, which was large, this is in agreement with ellipsometric studies of CuBTA films by Hobbins and Roberts [14] and Poling [5], but not with Brusic, et al. [17]. Poling [5] reports that CuBTA films formed near room temperature for 18 hours in aerated 0.02M BTA/distilled water, pH 5.0, produced 300 Å thick films, compared to about 100 Å in de-aerated solutions of the same type. Ogle and Poling [6] also report that the thinner films form with only minor decrease in thickness of the oxide layer proper. The effect of oxygen is to make the solution slightly corrosive to copper or, in this case, bronze. Based on ellipsometry results and on Poling's work, it is reasonable to conclude that the films produced in this study from 2 to 4 minute immersions were in the range of 100-200 Å. For these thin films, RAIR signal to noise ratios were generally poor and contributed to greater scatter in the data (see Fig. 4).

Figure 3, in which time is again plotted on a logarithmic scale, shows that the shapes of trendlines for film thickness in the 3.0% BTAH/ethanol and 1.5% BTAH/water series correspond well to those in Figure 2; this lends support to the application of Beer's Law. The results for sample films produced in 1.5% BTAH/ethanol were found to be unreliable and were omitted. The large error margin was attributed to two factors: (1) optical non-homogeneity in the films, viewed as stripes within the field of vision; and (2) the limitation of instrumental precision. The optical non-homogeneity was interpreted as due to uneven film thickness on a scale of about 200 angstroms. Unevenness in the films may ultimately reflect the underlying alloy, which is of course non-homogeneous in composition. It should also be noted that some deviation in a linear relationship between absorbance vs. film thickness might be expected from differences in film density or porosity, since RAIR absorbance represents the product of concentration and thickness.

Film density may in fact be somewhat unpredictable and thus be an important source of error in both the ellipsometry and RAIR data.

Film Growth

When viewed in more detail, RAIR results suggest that in near neutral, aerated solutions CuBTA films grow on rolled bronze in several distinct stages or cycles: 1) extremely rapid, initial film formation (within seconds); 2) marked slowing in film growth; 3) a second period of very rapid film growth, depending on solvent concentration; and 4) slow or negligible growth to a maximum. The initial growth stage can be extrapolated in Figure 4 as a near vertical line from 0 to 1 minute or less. The initially rapid formation of CuBTA films on air-exposed copper surfaces is well known from the literature; this film has been described as a monolayer produced by chemisorption of BTAH molecules on top of the natural oxide⁴ [6]. On bronze, the formation of CuBTA as well as ZnBTA may be uneven or discontinuous over oxides other than cuprite at this stage [18].

Subsequent nucleation and growth of CuBTA is generally accepted to occur by the movement of copper ions through the CuBTA film to the solid/solution interface, where a multi-layered complex forms by reaction with physisorbed BTAH. This corresponds to the second stage, which is seen in Figures 2, 4, and 5 to be rate dependent on the solution. Assuming the movement of copper ions in the CuBTA films is equivalent in all cases, the different growth rates observed for the three solutions may be explained as differences in the combined probability that the copper ions will meet a BTAH molecule at the film surface. Equilibrium surface coverage of physisorbed BTAH

on the CuBTA surface would be related to solution concentration. It is also reasonable to postulate the existence of a depleted layer of solvent at the CuBTA surface that would contribute to this picture by creating a concentration gradient in the solution and a driving force for BTAH molecules to pass through to the solid surface. A further explanation for observed differences in the rates of film growth could be variance in porosity of the developing films.

The plot in Figure 5, showing absorbance for immersion times up to 1 day, indicates what appears to be a second period of rapid increase in film thickness in the 3.0% BTAH/ethanol series near 1000 minutes of immersion. A similar increase in slope is indicated for 1.5% BTAH/ethanol-grown films between 8,000-10,000 minutes (Fig. 2). Thus the data appear to more correctly fit with two distinct slopes instead of one. Suggestion of a second CuBTA layer formation is supported in the literature by impedance studies, which have indicated a double layer structure [19]. This behavior may be interpreted as resulting from two rate determining steps separated in time, such as diffusion-controlled film formation followed by further copper ion diffusion into solution with eventual CuBTA precipitation and deposition. An alternative explanation would be that at some point during immersion and film formation a new corrosion phase is initiated, resulting in an increase in availability of copper ions and thus a rapid film formation stage.

The final data point for rolled bronze in 3.0% BTAH/ethanol at 60,036 minutes (Fig. 2) appears to mark the fourth stage, i.e., slow growth toward an apparent maximum. This appears likely to exist in all the solutions that were studied. This second stage of slow growth could correspond to a slower volume diffusion process of copper ions which

takes place after pores are closed in the CuBTA film, as suggested by Modestov, et al. [7].

It should be noted, however, that more than about 48 hours is not a realistic immersion time for a conservation treatment, and that the maximum protective efficiency of a CuBTA film may not coincide with maximum film thickness after a certain point. In fact, the rolled bronze sample appeared slightly oxidized after 42 days of immersion. This can be attributed to the corrosivity of oxygen in the BTA solution, which is also responsible for the apparent the inclusion of oxygen ligands in the Cu(I)BTA complex itself [15,20]. RAIR spectra of films after very long immersions in fact show evidence of Cu(II)BTA, as well as entrapment of uncomplexed BTAH molecules⁶. Trapped BTAH molecules were not eliminated either by additional rinsing or exposure in a 100 oven for 5 days. Oxidation of Cu(I)BTA to the cupric complex was also noted in films grown in the aqueous solution, although there is no evidence that this change has any detrimental effect on the inhibition properties. In addition, heating of CuBTA films on rolled bronze confirmed that the films are stable up to 155 °C, but that the substrate becomes very oxidized during heating, i.e., the film is highly permeable to oxygen in dry air heating. This concurs with reports in the literature [4].

RAIR experiments also showed that Cu(I)BTA films form on uncleaned rolled bronze in 1.5% BTAH/ethanol, and measure similar absorbance to that on the solvent-cleaned side. Earlier work showed that CuBTA films form over corroded copper surfaces containing copper chloride salts [15]. These results confirm the strong affinity of BTAH for copper and copper ions, in which complexing easily overcomes impurities and contamination. RAIR spectra were also obtained from rolled copper coupons which were

first coated with Incralac®, and from which this coating was then removed after about 1 week by solvent immersion and rinsing. RAIR of the copper after removal of the Incralac® clearly showed the presence of a CuBTA film remaining on the copper surface. The spectrum of this film (not shown) is similar to other CuBTA spectra, and exhibits absorbance at 745 cm^{-1} in the same range as spectra obtained for brushed BTAH on rolled bronze or from 1-4 minute immersions in BTAH solutions. These results indicate that BTAH is preferentially adsorbed to the copper surface during film formation of the Incralac®, so that a very thin film of Cu(I)BTA forms at the polymer/metal interface.

EIS

EIS results are shown in the Bode plot in Figure 6: impedance modulus values for the CuBTA films produced on polished bronze after 3 different immersions times in 3% BTA/ethanol. Values at 0.1 Hz confirm that the 4 minute film is significantly less protective in the electrolyte than the films formed after 1046 and 10,047 minutes. This correlates well with a difference in film thickness, as shown by RAIR results. The EIS results show little or no difference within experimental error in impedance between the latter two films. The fact that impedance of the 10,047 minute film is less than or equal to that of the 1046 minute film confirms RAIR results that indicate a limiting thickness is reached in CuBTA films from 3% BTA/ethanol near 1000 minutes. This immersion time coincides with possible deposition of a second CuBTA layer, and is close to the maximum film thickness. In general, EIS of these few samples supports the direct relationship between thickness in the CuBTA films and protective ability with respect to

an electrolyte that was chosen to correspond to major factors in outdoor exposure conditions [10].

Implications for Coated Outdoor Bronzes

In general, results provide a rationale for the lack of a recognizable effect of normal BTA pretreatments of coated bronzes exposed to the outdoors. What may be most significant in terms of conservation applications is proof that very thin films form almost immediately regardless of solution concentration or solvent for the short exposures that are typically used. Thus, because BTAH is normally brushed on, sprayed or otherwise exposed for relatively short periods of time, it is clear that CuBTA films formed in pretreatment or deposited through application of a coating containing BTA are quite thin regardless of substrate corrosion, contamination, or solution conditions. Films formed over corrosion have also been shown to be affected in composition by the underlying corrosion [2,15], although it is unclear how this may affect their inhibition efficiency. Coatings applied over CuBTA typically range in thickness from about 0.2 mils for wax to 4 mils for some synthetic coatings. Incralac® coatings are normally applied thinly to avoid an orange peel effect, and are in the range of 0.5-0.8 mils. Thus the CuBTA film is several orders of magnitude thinner than its overcoats.

In light of the severity of exposure conditions in outdoor environments, the effect of these thin CuBTA films as a physical barrier to such harsh environments may simply be negligible. It is interesting to speculate, however, that CuBTA films underneath an organic coating may have a more important function as a separating layer between the metal/metal salt and the coating. It has been well noted in the literature that copper ions

can accelerate the degradation of organic coatings, most likely through reaction with hydroperoxides [21].

The results of this study also imply that the effect of BTAH in treatment of bronzes may be greatly enhanced by longer exposure times to 3% BTAH/ethanol, e.g. 16-24 hours, if it is possible to do so without causing harm to the object. It should be noted that some studies have found optimal BTAH concentrations that were not necessarily the highest of the series under investigation [22]. Thus, it cannot be automatically assumed that 5% BTAH/ethanol would produce improved results in terms of protection. Furthermore, other investigations into CuBTA films have shown that slower growth generally produces denser and more highly polymerized films [4]. It is not clear if the rate of growth in the 3% BTAH/ethanol solution could compromise film quality in these ways or if the opposite is true. These hypotheses must therefore be tested in future work, which should include expanded EIS measurements.

CONCLUSIONS

Thin Cu(I)BTAH films form very rapidly on polished, rolled bronze in applications which model typical conservation treatments: either brushing, short immersion, or through the application of a coating of Incralac®. After longer exposures of 90 minutes or more in various solutions of BTAH, growth in CuBTA film thickness is markedly different depending on the BTAH concentration and the solvent. For immersion in 3% BTAH/ethanol, a maximum film thickness appears to exist and is approached near 1 week of immersion. It is likely that such a maximum exists for films

grown in neutral, mild, or organic BTAH solutions, although the position of the maximum may vary.

The growth patterns of CuBTA films on rolled bronze in the various solutions provide new evidence for step-wise, linear growth of Cu(I)BTA films that is time, concentration, and/or solvent dependent. In addition, the condition of the metal surface does not appear to greatly affect the thickness of the CuBTA film under normal conservation treatment conditions. These results suggest that the effectiveness of CuBTA pretreatments may be enhanced by controlling film thickness through solution concentration and time of exposure.

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NOTES

¹ A coating based on a methyl methacrylate copolymer and containing a small amount of BTAH and commonly used to protect copper alloys. Manufactured by Stan Chem, Inc., E. Berlin, Ct., U.S.A.

² Cf. *Metal Surface Characteristics Affecting Organic Coatings* (Federation Series of Coatings Technology, Blue Bell, Pa., August 1994) p. 63.

³ Other band assignments are discussed in an earlier paper [15].

⁴ A cuprous oxide layer formed on copper in air may be estimated from the literature to be about 25 Å.

⁵ Indicated in the shoulder at 1196 cm⁻¹, Fig. 1.

⁶ This was seen in notable shifts in the main triazo stretch bands near 1154 to 1207 and 1217 cm⁻¹, indicating the presence of BTAH and Cu(II)BTA, respectively.

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Figure 1
**RAIR Spectrum of CuBTA Formed on Rolled Bronze in 3% BTA/
ethanol after 1050 Minute Immersion.**

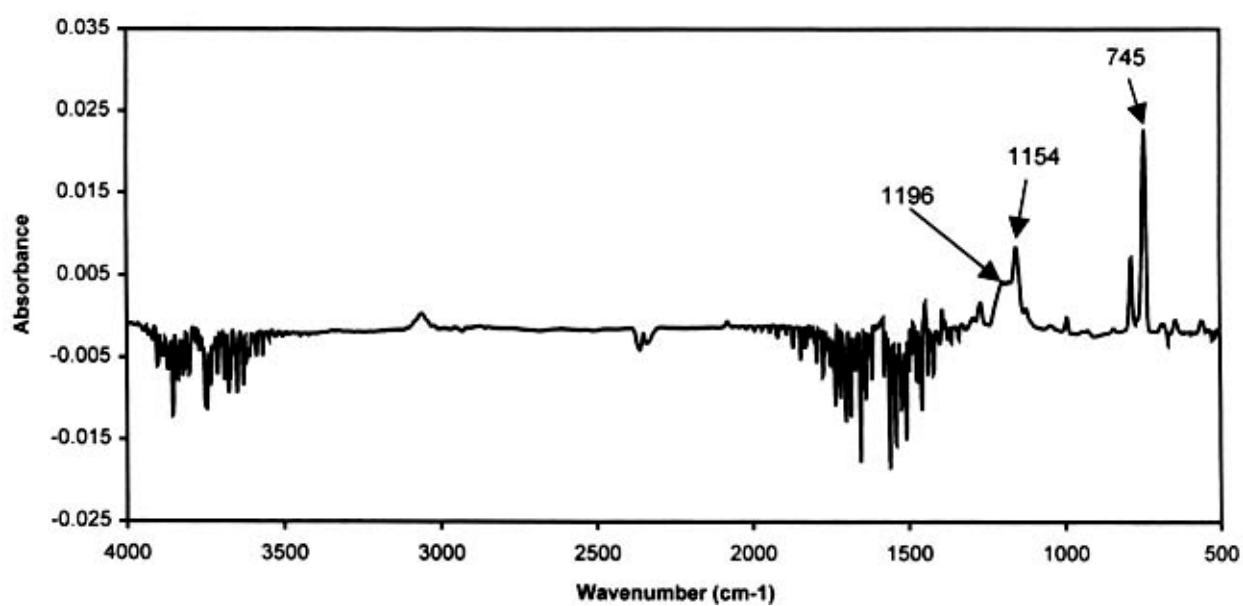


Figure 1
RAIR Spectrum of CuBTA Formed on Rolled Bronze
in 3% BTA/ ethanol after 1050 Minute Immersion

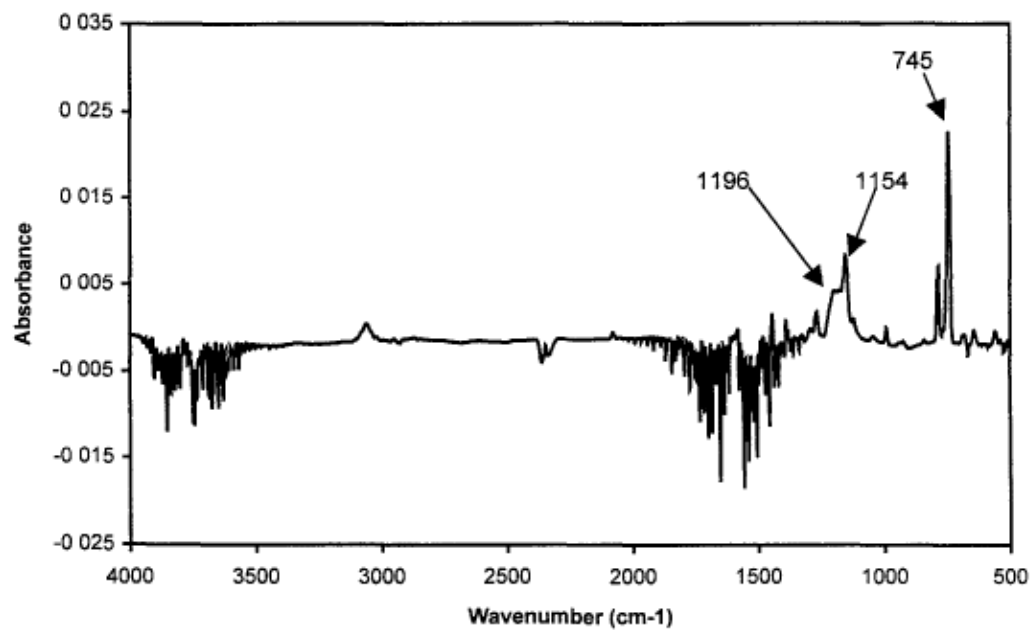


Figure 2
Absorbance at 745 cm⁻¹ vs. Time of Immersion
in Various Solutions for CuBTA Films on Rolled Bronze

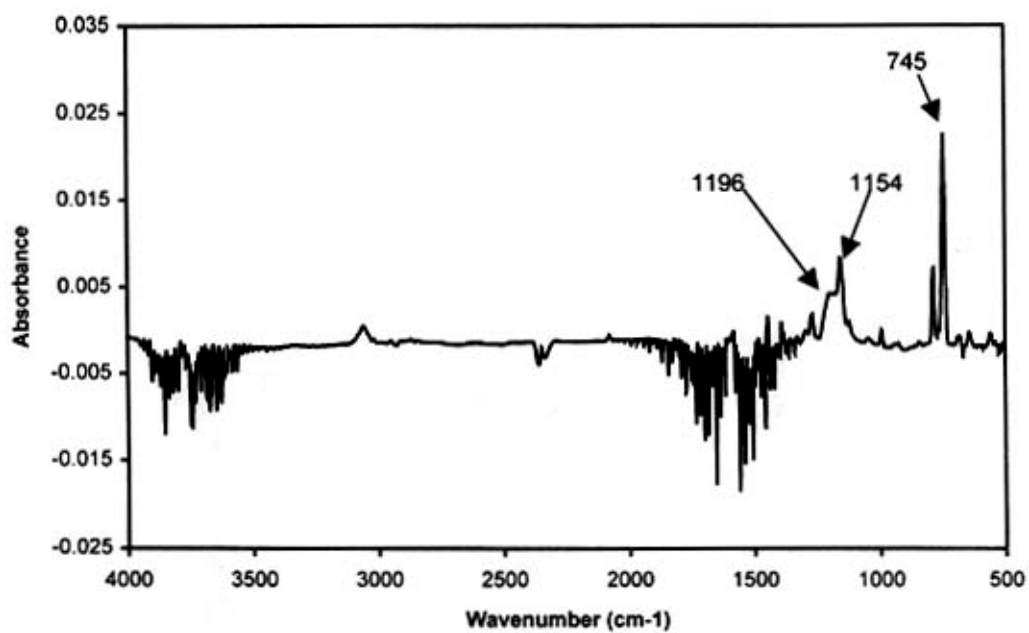


Figure 3
Film Thickness by Ellipsometry of CuBTA on Rolled Bronze
in 3% BTA/etOH and 1.5% BTA/water vs. Time of Immersion

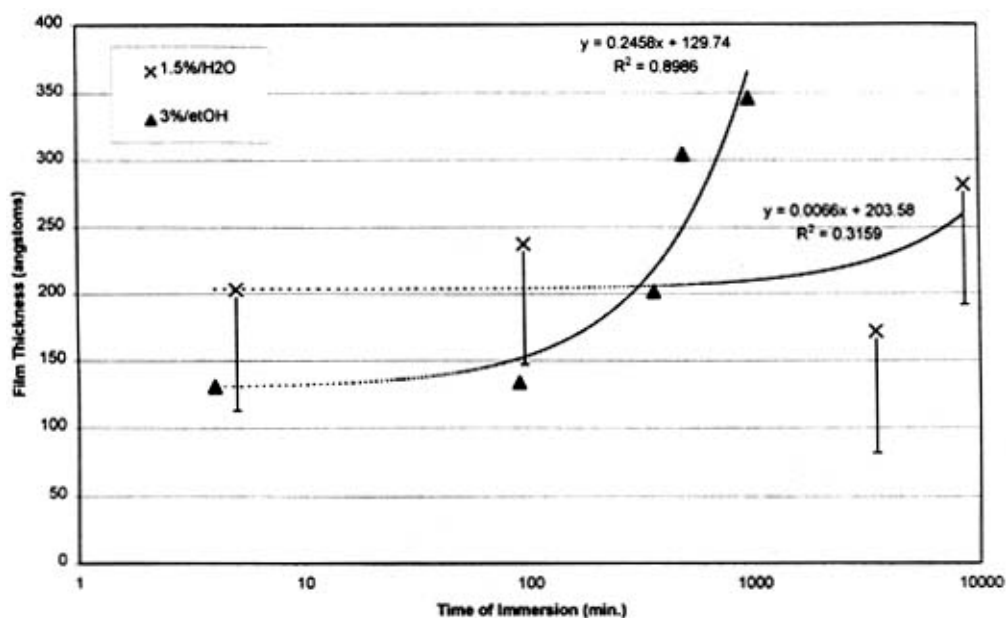


Figure 4
Absorbance at 745 nm vs. Time of Immersion
in Various Solutions for CuBTA Films on Rolled Bronze

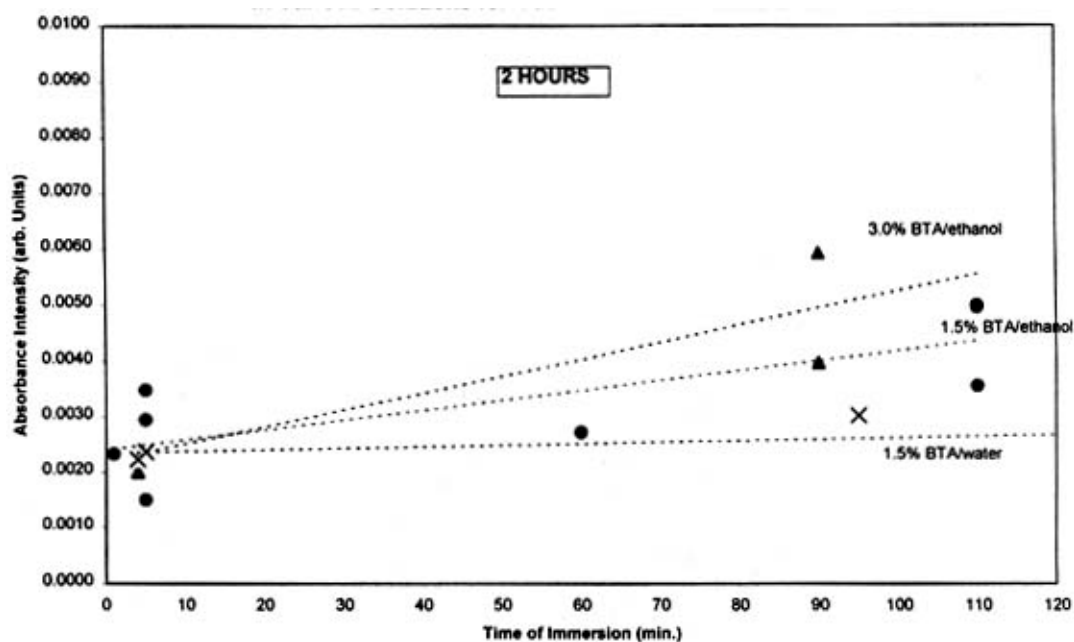


Figure 5
Absorbance at 745 cm⁻¹ vs. Time of Immersion
in Various Solutions for CuBTA Films on Rolled Bronze

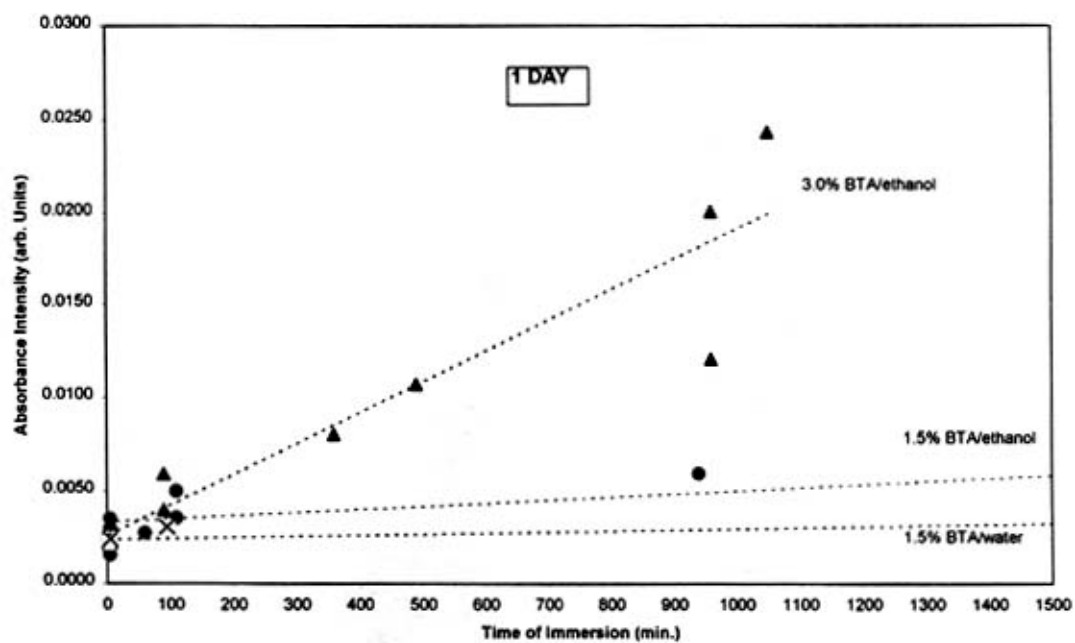
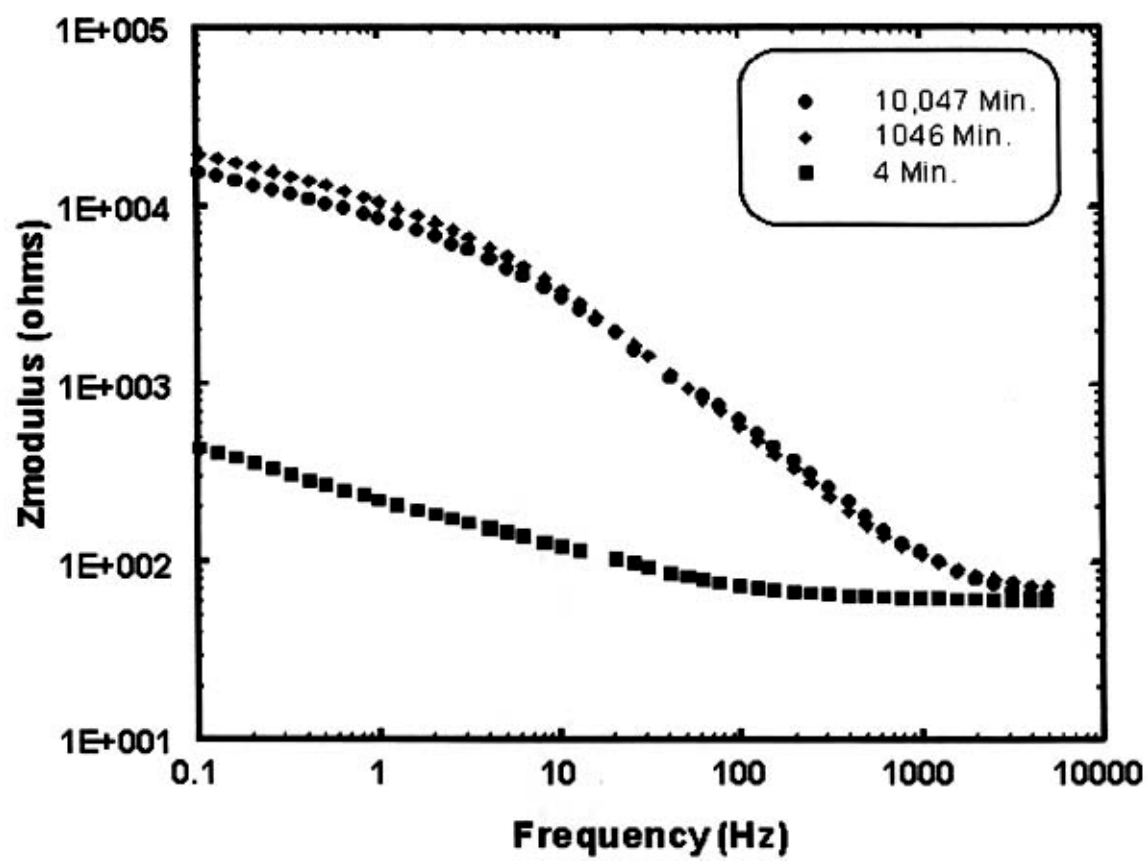


Figure 6

**Average Impedance modulus of CuBTA Films on Rolled Bronze
From Various Immersion Times in 3% BTA/ ethanol**



Appendix B

The Application of Digital Image Analysis to Performance Assessment of Coatings for Outdoor Bronze and Copper

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As part of a larger investigation into protective coatings for outdoor bronze sculpture and ornamentation at the National Gallery of Art in Washington, D.C., digital imaging and analysis were used to assess corrosion after weathering of coated bronze and copper substrates. To objectively judge the performance of each coating, a series of test methods were implemented, including digital image analysis. The purpose of the digital image analysis was to improve the accuracy of the ASTM methods for determination of linear creepage corrosion at a scribe mark and percent overall corrosion on the surface of the substrates.

In order to observe differences in coating performance and its dependency on the substrate's condition and preparation, five coatings were applied to the following substrates: 1) polished, cast bronze, 2) artificially patinated, cast bronze, 3) 50-year-old, naturally patinated copper roof, and 4) walnutshell-blasted, 50-year-old copper roof. These samples were exposed to either six months accelerated artificial weathering, or one-year natural outdoor weathering. The surface variations on the sample substrates posed particular problems for the definition of corrosion by digital methods.

Photographs of the samples were captured and then scanned as 32-bit images. The digital images created a superb record of the condition of the samples shortly after completion of weathering and remain valuable for future study. IPLab for Macintosh version 3.2, marketed by Scanalytics, Inc., was used to quantify the amount of corrosion at the scribemark and overall on each substrate. Algorithms for measuring scribemark corrosion were readily determined and succeeded well. This method was a significant improvement over the ASTM D1654 method, which uses the unaided eye or low magnification while manually measuring the creepage corrosion along the scribemark. In the assessment of overall percent corrosion, the wide range of surface coloration and corrosion characteristics on the four different substrates caused difficulty in the digital image analysis.

The combination of the corrosion, natural surface mottling, and uneven coloration of the samples rendered the systems too complex to accurately define the corrosion by any algorithm written for this program, except in the case of polished bronze. While good correlation between the digital analysis and that of the human eye existed for overall corrosion on the polished bronze substrates, correlation between the two methods was poor on the more complex surfaces of the remaining substrates. Therefore, with the aid of the digital images, the ASTM D610 standard and method for percent overall corrosion was ultimately used in the final performance ratings. The image of each substrate was enlarged on the computer monitor, and a defined area on each substrate was compared to the method of determination in ASTM D6 10. Recommendations for the use of digital imaging analysis in future experiments will be discussed.